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Ferrous Metals and Their Alloys

The ferrous metals are defined as the three upper transition metals of group VIIIB (8, 9, and 10) of Mendeleev's periodic chart, that is, iron (Fe), cobalt (Co), and nickel (Ni), along with chromium (Cr) and manganese (Mn), despite the fact that these two metals belong to groups VIB(6) and VIIB(7), respectively. Manganese is included in this chapter because it has an important role in iron- and steel-making, while chromium, owing to its refractory behavior, will be described in the chapter on refractory metals (see Section 4.3.8). The selected physical and chemical properties of these five elements are listed in Table 2.1.

2.1 Iron and Steels

2.1.1 Description and General Properties

Iron [7439-89-6], chemical symbol Fe, atomic number 26, and relative atomic mass 55.845(2), is the first element of the upper transition metals of group VIIIB(8) of Mendeleev's periodic chart. The word iron comes from the Anglo-Saxon *iren*, while the symbol Fe and words such as ferrous and ferric derive from the Latin name of iron, *ferrum*. Pure iron is a soft, dense (7874 kg.m^{-3}), silvery-lustrous, magnetic metal with a high melting point (1535°C). In addition, when highly pure iron has both a good thermal conductivity ($80.2 \text{ W.m}^{-1}.\text{K}^{-1}$) and a low coefficient of linear thermal expansion ($11.8 \text{ }\mu\text{m/m.K}$), it is a satisfactory electric conductor ($9.71 \text{ }\mu\Omega.\text{cm}$).

Table 2.1. Selected properties of iron, cobalt, nickel, chromium, and manganese						
Properties at 298.15 K (unless otherwise specified)						
Designations	Iron (Ferrum)					
	Chemical symbol (IUPAC)	Fe	Cobalt	Nickel	Chromium	Manganese
Natural occurrence and economics	Chemical abstract registry umber [CARN]	[7439-89-6]	[7440-48-4]	[7440-02-0]	[7440-47-3]	[7439-96-5]
	Unified numbering system [UNS]	[F00001]	[R30001]	[N02200]	[R20001]	[M20001]
	Earth's crust abundance (mg.kg ⁻¹)	56300	25	84	102	950
	Seawater abundance (mg.kg ⁻¹)	20 × 10 ⁻⁴	0.2 × 10 ⁻⁴	5.6 × 10 ⁻⁴	3 × 10 ⁻⁴	2 × 10 ⁻⁴
	World estimated reserves (R/tonnes)	110 × 10 ⁹	n.a.	70 × 10 ⁶	1 × 10 ⁹	700 × 10 ⁶
	World annual production of metal in 2004 (P/tonnes)	940 × 10 ⁶	35,000	1.033 × 10 ⁶	30,000	100,000
	Price of pure metal in 2004 (C/\$US.kg ⁻¹) (purity in wt.%)	0.350 (98)	55–57 (99.8)	12.85–13.35 (99.8)	10.25–10.65 (99.4)	1.3–1.4 (99.7)
	Atomic number (Z)	26	27	28	24	25
	Relative atomic mass A _r (¹² C = 12.000) ¹	55.845(2)	58.933200(9)	58.6934(2)	51.9961(6)	54.938049(9)
	Electronic configuration (ground state)	[Ar]3d ⁶ 4s ²	[Ar]3d ⁷ 4s ²	[Ar]3d ⁸ 4s ²	[Ar]3d ⁵ 4s ¹	[Ar]3d ⁵ 4s ²
	Fundamental ground state	⁵ D ₄	⁴ F _{9/2}	³ F ₄	⁷ S ₃	⁶ S _{5/2}
	Atomic or Goldschmidt radius (pm)	126	125	125	129	137
Atomic properties	Covalent radius (pm)	116	116	115	118	118
	Electron affinity (E _a /eV)	0.151	0.662	1.160	0.666	n.a.
	First ionization energy (E _i /eV)	7.9024	7.8810	7.6398	6.76664	7.43402
	Second ionization energy (eV)	16.1878	17.083	18.16884	16.4857	15.63999
	Third ionization energy (eV)	30.652	33.50	35.19	30.96	33.668
	Electronegativity χ _a (Pauling)	1.83	1.88	1.91	1.66	1.55
	Electronegativity χ _s (Allred and Rochow)	1.64	1.75	1.75	1.56	1.60
	Electron work function (W _f /eV)	4.06	4.30	4.40	3.72	3.72
	X-ray absorption coefficient CuK _{α,β} ((μ/ρ) /cm ² ·g ⁻¹)	308	313	45.7	260	285
	Thermal neutron cross section (σ _a /10 ⁻²⁸ m ²)	2.56	37.2	37.2	3.1	13.3
	Isotopic mass range	49–63	35–64	53–67	45–57	49–62
	Isotopes (including natural and isomers)	16	17	14	13	15

Table 2.1. (continued)

Properties at 298.15 K (unless otherwise specified)		Iron (Ferrum)	Cobalt	Nickel	Chromium	Manganese
Thermal and thermodynamic ³ properties [293.15K]	Temperature of fusion (T_f /K)	1808.05 (1534.90)	1728.05 (1454.90)	1726.05 (1452.90)	2130.05 (1856.90)	1517.05 (1243.90)
	Melting point ($m.p.$ /°C)					
	Temperature of vaporization (T_v /K)	2749.9 (2476.75)	3143.05 (2869.90)	3005.05 (2731.90)	2945.05 (2671.90)	2335.05 (2061.90)
	Boiling point ($b.p.$ /°C)					
	Thermal conductivity (k /W.m ⁻¹ .K ⁻¹)	80.2	99.2	90.7	93.7	7.82
	Volume expansion on melting (/vol.%)	+3.5	+3.5	+4.5	+10.15	+1.7
	Coefficient of linear thermal expansion (α /10 ⁻⁶ .K ⁻¹)	11.8	13.4	13.3	6.2	21.7
	Specific heat capacity (c_p /J.kg ⁻¹ .K ⁻¹)	447	421	471	459.8	479
	Spectral normal emissivity (650 nm)	0.35 (1200°C)	0.37 (1200°C)	0.34 (1000°C)	0.34 (1000°C)	0.59 (1200°C)
	Standard molar entropy (S_{298}^0 /J.mol ⁻¹ .K ⁻¹)	27.280	30.067	29.796	23.618	32.010
	Latent molar enthalpy of fusion (ΔH_{fus} /kJ.mol ⁻¹) (Δh_{fus} /kJ.kg ⁻¹)	15.2 (272)	15.5 (263)	17.16 (292)	20.90 (402)	12.058 (219)
	Latent molar enthalpy of vaporization (ΔH_{vap} /kJ.mol ⁻¹) (Δh_{vap} /kJ.kg ⁻¹)	340.4 (6095)	382.4 (6489)	377.5 (6431)	348.78 (6708)	231.1 (4207)
	Latent molar enthalpy of sublimation (ΔH_{sub} /kJ.mol ⁻¹)	398.6 (7138)	425 (7211)	429.6 (7320)	397 (7635)	291 (4267)
	Molar enthalpy of formation (ΔH_f^0 /kJ.mol ⁻¹) (oxide)	-272.0 (FeO)	-237.7 (CoO)	-240.6 (NiO)	-1140 (Cr ₂ O ₃)	-385.2 (MnO)
Electrical and electrochemical properties	Electrical resistivity (ρ /μΩ.cm)	9.71	6.24	6.844	12.7	144
	Temperature coefficient of electrical resistivity (0–100°C) (/10 ⁻³ .K ⁻¹)	6.51	6.60	6.92	2.14	0.4
	Pressure coefficient of electrical resistivity (/MPa ⁻¹)	-23.4 × 10 ⁻⁵	-9.04 × 10 ⁻⁵	+1.82 × 10 ⁻⁵	-17.3 × 10 ⁻⁵	-35.4 × 10 ⁻⁵
	Hall coefficient at 293.15 K (R_H /nΩ.m.T ⁻¹) [0.5 T < B < 2.0 T]	+0.080	+0.360	-0.060	+0.363	+0.084
	Seebeck absolute coefficient (e_s /μV.K ⁻¹) (thermoelectric power)	-51.34	+17.5	-18.0	n.a.	n.a.
	Thermoelectronic emission constant (A /kA.m ⁻² .K ⁻²)	260	410	300	n.a.	n.a.
	Thermoelectric power vs. platinum (Q_{AB} /mV vs. Pt) (0–100°C)	+1.89	-1.33	-1.48	+2.20	+0.70

Magnetic and optical properties	Nernst standard electrode potential (E/V vs. SHE)	$\text{Fe}^{2+}/\text{Fe}^0$ −0.440	$\text{Co}^{2+}/\text{Co}^0$ −0.277	$\text{Ni}^{2+}/\text{Ni}^0$ −0.257	$\text{Cr}^{3+}/\text{Cr}^0$ −0.740	$\text{Mn}^{2+}/\text{Mn}^0$ −1.170
	Hydrogen overvoltage (η/mV) with $[\text{H}^+] = 1\text{M}$, and $j_c = -200\text{ A}\cdot\text{m}^{-2}$)	425	n.a.	384	n.a.	n.a.
	Mass magnetic susceptibility ($\chi_m/10^{-9}\text{ kg}^{-1}\text{ m}^3$) (at 295 K)	Ferromagnetic	Ferromagnetic	Ferromagnetic	+44.50	+121
	Curie temperature ($T_{\text{Curie}}/\text{K}$)	1043	1394.15	633	$T_{\text{Neel}} = 311$	$T_{\text{Neel}} = 100$
	Reflective index under normal incidence (650 nm)	0.563	0.675	0.659	0.644	0.606

¹ Standard atomic masses from: Loss, R.D. (2003) Atomic weights of the elements 2001. *Pure Appl. Chem.*, 75(8), 1107–1122.

² Thermodynamic properties from: Chase, Jr., M.W. (1998) *NIST-JANAF Thermochemical Tables*, 4th ed., Part I & II. J. Phys. Chem. Reference Data, Monograph No. 9 published by Springer, Berlin Heidelberg New York.

Table 2.2. Reactions of pure iron metal with acids

Acid	Soln.	Chemical reaction scheme	Notes
Hydrochloric acid (HCl)	Conc.	$\text{Fe}^0 + 2\text{HCl} \longrightarrow \text{Fe}^{2+} + 2\text{Cl}^- + \text{H}_2(\text{g})$	Dissolves with effervescence
Sulfuric acid (H_2SO_4)	Dil.	$\text{Fe}^0 + \text{H}_2\text{SO}_4 \longrightarrow \text{Fe}^{2+} + \text{SO}_4^{2-} + \text{H}_2(\text{g})$	Dissolves with effervescence
	Conc. cold	No reaction	Does not dissolve
	Conc. hot	$2\text{Fe}^0 + 6\text{H}_2\text{SO}_4 \longrightarrow 2\text{Fe}^{3+} + 3\text{SO}_4^{2-} + 3\text{SO}_2(\text{g}) + 6\text{H}_2\text{O}$	Dissolves
Nitric acid (HNO_3)	Dil. cold	$4\text{Fe}^0 + 10\text{HNO}_3 \longrightarrow 4\text{Fe}^{2+} + \text{NH}_4^+ + 9\text{NO}_3^- + 3\text{H}_2\text{O}$	Dissolves
	Dil. hot	$\text{Fe}^0 + 4\text{HNO}_3 \longrightarrow \text{Fe}^{3+} + 3\text{NO}_3^- + \text{NO}(\text{g}) + 2\text{H}_2\text{O}$	Dissolves readily
	Conc. cold	$3\text{Fe}^0 + 16\text{HNO}_3 + 16\text{H}^+ \longrightarrow \text{Fe}_3\text{O}_4(\text{surface}) + 8\text{NO}_2(\text{g}) + 8\text{H}_2\text{O}$	Does not dissolve due to passivation by Fe_3O_4

At room temperature, highly pure iron crystallizes into a body-centered cubic (bcc) space lattice. From a mechanical point of view, pure iron exhibits a high elastic Young's modulus of 208.2 GPa, with a Poisson ratio of 0.291, but it is malleable and can be easily shaped by hammering. Other mechanical properties such as yield and tensile strength strongly depend on interstitial impurity levels and type of crystal space lattice structure. Pure iron is a soft ferromagnetic material with a saturation magnetization M_s of $1.71 \times 10^6 \text{ A.m}^{-1}$ and a remanent magnetic induction of 0.8 T and a low coercivity of 80 A.m^{-1} . These properties explain why iron cores are extensively used in electromagnets. However, the high hysteresis core losses of 500 W.kg^{-1} act to decrease its electric resistivity by alloying it with silicon in order to be suitable in transformers. However, iron loses its ferromagnetism above its Curie temperature of 769°C (1043 K) and becomes paramagnetic. Natural iron is composed of four stable nuclides— ^{54}Fe (5.845 at.%), ^{56}Fe (91.754 at.%), ^{57}Fe (2.1191 at.%), and ^{58}Fe (0.2819 at.%)—and the element has a thermal neutron cross section of 2.56 barns. From a chemical point of view, pure iron is an active metal, and hence it rusts (i.e., oxidizes) when put in contact with moist air, forming a porous nonprotective hydrated ferric-oxide layer. In addition, pure iron readily dissolves in several diluted strong mineral acids such as hydrochloric and sulfuric acids, but it is not attacked by concentrated sulfuric or nitric acids due to the passivation by a scale of insoluble magnetite (Fe_3O_4). The major reactions of iron metal with the most common acids are summarized in Table 2.2.

Various types of relatively pure or high-purity iron can be found on the market, although only a few of them are used as structural material. Most commercial irons, except *ingot iron* and *electrolytic iron*, contain perceptible quantities of carbon, which affects their properties. Other common high-purity iron types include *reduced irons* and *carbonyl iron* (powders).

Prices (2006). Pure iron metal (i.e., 99.99 wt.% Fe) is priced US\$2.205/kg (i.e., US\$1.00/lb.), while common iron (99 wt.% Fe) is priced US\$0.350/kg (US\$0.159 US\$/lb.).

2.1.2 Phase Transitions and Allotropism of Iron

The wide variations in the properties of iron and iron alloys must be related to the existence of pure solid iron in more than one phase, i.e., several crystallographic structures. This characteristic of many chemical elements including iron is called *allotropism*. Allotropism must not be confused with the term applied to a pure compound (e.g., a molecule or an alloy) that exhibits several crystal lattices and is called *polymorphism*. The temperature at which a change in

the crystal structure occurs under constant pressure is called the phase **transition temperature** or **critical point**. These phase changes occurring in the phase diagram of iron can be accurately pointed out by means of X-ray diffraction, thermal analysis, and dilatometry techniques. Under atmospheric pressure, pure iron metal exhibits the four allotropes as follows and a high-pressure form.

Alpha-iron (α -Fe). Between room temperature and a transition temperature of 769°C, pure iron exhibits a body-centered cubic (bcc) crystal lattice ($a = 286.645$ pm at 25°C). Alpha-iron is a soft, ductile metal with a density of 7875 kg.m^{-3} . Alpha-iron is also ferromagnetic, with a saturation magnetization at room temperature of $220 \text{ A.m}^2.\text{kg}^{-1}$, and the cubic anisotropy constants are $K_1 = 4.7 \times 10^4 \text{ J.m}^{-3}$ and $K_2 = 1.5 - 3.0 \times 10^4 \text{ J.m}^{-3}$. Carbon exhibits a poor solubility in alpha-iron with a maximum content of 0.025 wt.% C at 723°C. It is important to note that the word **ferrite** describes a solid solution of carbon into alpha-iron, though it is sometimes improperly used to describe alpha-iron (Section 2.1.9):

α -Fe (bcc, ferromagnetic) \longrightarrow β -Fe (bcc, nonmagnetic) [$T_t = 769^\circ\text{C}$; $\Delta H_{\alpha\beta} = 0 \text{ kJ.mol}^{-1}$].

Beta-iron (β -Fe). When heated above its Curie temperature of 769°C, alpha-iron loses its ferromagnetic properties but retains its body-centered cubic structure (i.e., second-order transition). This particular form of iron is called beta-iron, which is considered a different allotropic form owing to its paramagnetic properties. However, because no changes in the crystal lattice structure occurs, it is customary to consider it nonmagnetic alpha-iron:

β -Fe (bcc, nonmagnetic) \longrightarrow γ -Fe (fcc, nonmagnetic) [$T_t = 910^\circ\text{C}$; $\Delta H_{\beta\gamma} = +0.9 \text{ kJ.mol}^{-1}$].

Gamma-iron (γ -Fe). At 910°C, the crystallographic structure of iron changes into a face-centered cubic (fcc) structure ($a = 364.680$ pm at 916°C). At this transition temperature, a considerable absorption of latent heat occurs due to the endothermic reaction, and the volume of the iron unit cell expands to 25 vol.%. Gamma-iron is nonmagnetic and has

Table 2.3. Physical properties of four iron allotropes and high-temperature forms

Properties (SI units)	α -Fe	β -Fe	γ -Fe	δ -Fe	ϵ -Fe
Crystal structure	bcc	bcc	fcc	bcc	hcp
Lattice parameters (/pm)	$a = 286.645$	$a = 286.645$	$a = 364.680$	$a = 291.35$	$a = 248.5$ $c = 399.0$
Space group (Hermann–Mauguin)	Im3m	Im3m	Fm3m	Im3m	P6 ₃ /mmc
Pearson symbol	cI2	cI2	cI4	cI2	hP2
Strukturbericht	A2	A2	A1	A2	A3
Transition temperature (T/K)	1042	1183	1665	1812	$P > 13 \text{ GPa}$
Latent enthalpy of transition ($\Delta H_t/\text{kJ.mol}^{-1}$)(kJ.kg^{-1})	0.00 ()	+0.900 ()	+0.837 ()	+13.807 ()	(?)
Density ($\rho/\text{kg.m}^{-3}$)	7875	7875	7648	7357	(?)
Coefficient of linear thermal expansion ($\alpha/10^{-6} \text{ K}^{-1}$)					
Thermal conductivity ($k/\text{W.m}^{-1}.\text{K}^{-1}$)					
Specific heat capacity ($c_p/\text{J.kg}^{-1}.\text{K}^{-1}$)					
Electrical resistivity ($\rho/\mu\Omega.\text{cm}$)					

a lower density (7648 kg.m^{-3}) than low-temperature phases, which have a body-centered cubic structure. Gamma-iron dissolves a nonnegligible amount of carbon, e.g., 1.7 wt.% C, at 1150°C . It is important to note that the word **austenite** describes a solid solution of carbon in gamma-iron, though it is also used improperly for denoting gamma-iron (Section 2.1.9):

$\gamma\text{-Fe}$ (fcc, nonmagnetic) $\rightarrow \delta\text{-Fe}$ (bcc, magnetic) [$T_i = 1392^\circ\text{C}$; $\Delta H_\gamma = +0.837 \text{ kJ.mol}^{-1}$].

Delta-iron ($\delta\text{-Fe}$). At 1392°C , a third transformation occurs and the face-centered cubic lattice reverts to a body-centered cubic form ($a = 293.22 \text{ pm}$) with a density of 7357 kg.m^{-3} , which again becomes ferromagnetic. Finally, at a melting point of 1535°C , iron absorbs the latent heat required for fusion and becomes liquid (i.e., molten iron):

$\delta\text{-Fe}$ (bcc, ferromagnetic) $\rightarrow \text{Fe}$ (liquid) [$T_m = 1535^\circ\text{C}$; $\Delta H_m = +13.807 \text{ kJ.mol}^{-1}$].

Epsilon-iron ($\epsilon\text{-Fe}$). Scientists subjecting iron to high pressure using diamond anvil experiments have discovered that there also exists a high-pressure form of metallic iron called epsilon-iron ($\epsilon\text{-Fe}$) that forms only above a pressure of 13 GPa. Epsilon-iron exhibits the hexagonal close-packed (hcp) structure. Despite the fact that this phase has no effect on the metallurgy of iron, the phase is of particular interest for geophysicists because it seems to be one of the major constituents of the dense and solid inner core of the Earth.

2.1.3 Metallographic Etchants for Iron and Steels

The recipes for preparing the most common etchants used to reveal the microstructure of iron and steel are listed in Table 2.4.

2.1.4 History

Iron has been known since prehistoric times, and no other element has played a more important role in human material progress. Iron beads dating from around 4000 B.C. were no doubt of meteoritic origin, and later samples produced by reducing iron ore with charcoal were not cast because adequate temperatures were not attainable without use of some form of bellows. Instead, the spongy material produced by low-temperature reduction would have had to be shaped by prolonged hammering. It seems that iron was first smelted by Hittites sometimes in the third millennium B.C., but the value of the process was so great that its secret was carefully guarded, and it was only with the fall of the Hittite empire around 1200 B.C. that the knowledge was dispersed and the “Iron Age” began. In more recent times the introduction of coke as the reductant had far-reaching effects and was one of the major factors in the initiation of the Industrial Revolution.

2.1.5 Natural Occurrence, Minerals, and Ores

Because nuclides of iron are especially stable with the highest binding energy per nucleon (e.g., $-8.79 \text{ MeV/nucleon}$ for ^{56}Fe), its cosmic abundance is particularly high, and it is thought to be the main constituent of the Earth’s inner core as an iron-nickel alloy (see Section 13.2), named for its chemical composition NiFe by the Austrian geophysicist Suess. The relative Earth’s crust abundance is about 5.63 wt.% Fe; hence it is the fourth most abundant element after oxygen, silicon, and aluminum and the second most abundant metal after aluminum.

Table 2.4. Common metallographic etchants for iron and steels

Etchant	Composition	Description
Nital	99-90 cm ³ EtOH 1-10 cm ³ HNO ₃	Nital is the most common etchant for steels. Do not store nital with more than 3 wt.% nitric acid in ethanol due to decomposition. Use by immersion or swabbing applying a low pressure.
Picral	100 cm ³ EtOH 4 g picric acid	Picral is better than nital for revealing annealed microstructures. Does not reveal ferrite grain boundaries. Etch by immersion or swabbing.
Vilella's reagent	100 cm ³ EtOH 5 cm ³ HCl 1 g picric acid	Vilella's reagent is good for higher alloyed steels, tool steels, and martensitic stainless steels. Etch by immersion or swabbing.
Carpenter's reagent	85 mL EtOH 15 mL HCl	Etch for duplex stainless steels. Immerse specimens 15–45 min to reveal the grain and phase boundaries in duplex stainless steels.
Klemm's I reagent	50 cm ³ saturated Na ₂ S ₂ O ₃ 1 g K ₂ S ₂ O ₅	Klemm's I tint etch colors ferrite strongly; also colors martensite and bainite, but not carbides or retained austenite. Use by immersion only until the surface is colored.
Alkaline picrate	100 cm ³ H ₂ O 25 g NaOH 2 g picric acid	Alkaline sodium picrate must be used at 80–100°C by immersion only. Colors cementite (Fe ₃ C) and M ₆ C carbides.
Electrolytic etching	100 cm ³ H ₂ O 20 g NaOH	Electrolytic etching for stainless steels. Specimen polarized as anode (+) under a cell voltage of 3 V during 10 s to color ferrite (tan or light blue) and sigma (orange) but does not affect austenite.
Murakami's reagent	100 cm ³ H ₂ O 10 g NaOH (KOH) 10 g K ₃ Fe(CN) ₆	Used to color ferrite and sigma (80–100°C for up to 3 min) in stainless steels. At room temperature will not color ferrite but will color certain carbides. At high temperatures, colors ferrite, sigma, and carbides, but not austenite.
Beraha's sulfamic acid reagent	100 cm ³ H ₂ O 3 g K ₂ S ₂ O ₅ 2 g sulfamic acid 0.5-1 g NH ₄ HF ₂	Color phases in highly alloyed tool steels and martensitic stainless steels. Use by immersion only, 30–180 s in a freshly prepared solution. Due to ammonium hydrogen fluoride PTFE or PP beaker and tongs must be used.
Beraha's reagent	85 cm ³ H ₂ O 15 cm ³ HCl 19 g K ₂ S ₂ O ₅	Beraha-type etch for duplex stainless steels in a freshly prepared solution. Use by immersion until surface is colored. Colors ferrite but not austenite.

Native metallic iron, owing to its chemical reactivity to oxygen, occurs rarely free in nature. **Native iron** occurs either as telluric iron or meteoric iron. **Terrestrial iron**, also called **telluric iron** to distinguish it from native iron of meteoric origin, is found in masses occasionally of great dimensions weighing up to 80 tonnes, as well as small embedded particles of a few grams in basalts such as at Blaafjeld, Ovivak on Disco Island (Western Greenland). Terrestrial iron usually exhibits a low carbon content (i.e., between 0.2 and 0.7 wt.% C) and also contains 0.5 to 4 wt.% Ni with 1000 to 4000 ppm wt. Co. Moreover, nickeliferous metallic iron, called **awaruite** (FeNi₂, cubic), occurs in the drift of the George River, which empties into Awarua Bay on the west coast of the South Island of New Zealand, while **josephinite** (FeNi₃) occurs in alluvial deposits such as stream gravels in Oregon, USA. **Meteoric iron – native meteoric iron** is of extraterrestrial origin coming from falling meteorites. In most cases, it forms the entire mass of the meteorite, i.e., iron meteorites or siderites, it forms a spongy cellular matrix with embedded grains of silicates such as olivine, i.e., lithosiderites or siderolites, and finally it is disseminated through a silicate matrix, i.e., stony meteorites or litholites. Meteorites are described in more detail in Section 13.8.

Iron in nature is essentially combined with other chemical elements in a wide variety of mineral species found in igneous, metamorphic, or sedimentary rocks or as weathering products of various primary iron-bearing materials (laterites) and also in other geologic materials (e.g., soils). However, sedimentary deposits account for 80% of the world reserves of iron. Among them, the most widely distributed iron-bearing minerals of economic importance are oxides such as *hematite* [Fe_2O_3 , rhombohedral with 70 wt.% Fe], *magnetite* [Fe_3O_4 , cubic with 72.4 wt.% Fe], and *limonite* [$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, orthorhombic with 63 wt.% Fe], the carbonate *siderite* [FeCO_3 , rhombohedral with 48.2 wt.% Fe], and the two sulfides *pyrite* [FeS_2 , cubic] and *marcasite* [FeS_2 , orthorhombic], both with 47 wt.% Fe. Of these minerals only oxides are commonly used as iron ores for ironmaking.

Iron ore deposits have a wide range of formation in geologic time as well as a wide geographic distribution. They are found in the oldest known rocks of the lithosphere, with an age in excess of 2.5 Ga, as well as in rock units formed in various subsequent ages; in fact, iron ores are still forming today in areas where iron hydroxides are being precipitated in marshy areas and where magnetite placers are being formed on certain beaches. Many thousands of iron occurrences are known throughout the world. They range in size from a few tonnes to many hundreds of millions of tonnes. Many of the world's largest deposits of iron ore are located in Precambrian formations. These deposits account for 90% of world reserves. These iron ores exhibit an elevated Fe/Si ratio of 0.7 and are rich in aluminum and phosphorus and sometimes manganese.

Commercially profitable extraction requires iron ore deposits that have a raw ore with more than 30 wt.% Fe. Although certain exceptional iron ores contain as much as 66 wt.% Fe, the major commercial iron ores usually contain 50 to 60 wt.% Fe. In addition, the quality of the iron ore is influenced by the type of inert gangue materials. In addition to iron content, the amount of silica, phosphorus, and sulfur-bearing compounds is also important because they strongly affect the steelmaking process.

Although iron ore production is widely distributed, i.e., occurring in ca. 50 countries, the bulk of the world production comes from just a few countries. For instance, in 2004, the 10 most important iron-ore-producing countries were, in decreasing order of mining production, Brazil, Australia, India, China, Russia, Ukraine, South Africa, Canada, Venezuela, and Sweden (Table 2.5 for more details). Together, these countries produce 70% of the world total. Note that China was the largest producer of crude ore in 2002, but, owing to the low iron content of its ore of about 32 wt.% Fe, it must be concentrated to 60 wt.% Fe or more. Hence its usable ore production is ranked well below that of both Brazil and Australia for that year.

Table 2.5. Major iron-ore-producing countries (2002)

Rank	Producing country	Major iron ore districts and ore type	Production (/10 ⁶ tonnes)
1	Brazil	<i>Quadrilátero Ferrífero</i> (Minas Gerais): Precambrian marine sedimentary deposits (35–60 wt.% Fe). Carajas ore district: Precambrian metamorphic ore beds enriched by weathering (60–65 wt.% Fe)	239.4
2	Australia	Hamersley Range in the Pilbara district (WA): Precambrian banded sedimentary deposits heavily metamorphized (itabirite)	187.2
3	China	Provinces of Liaoning and Hebei; ores of itabirite type	108.8 ³
4	India	Bihar (State of Orissa) and Mahya (India Pradesh) Precambrian sedimentary rocks	86.4
5	Russia	Kursk (Western Siberia); magnetite ore bodies with iron and zinc sulfides	84.2

³ Adjustment of the original value of 231 million tonnes to account the lower average mined grade.

Table 2.5. (continued)

Rank	Producing country	Major iron ore districts and ore type	Production (/10 ⁶ tonnes)
6	Ukraine	Krivoi Rog; Precambrian sedimentary ores	58.9
7	United States	Lake Superior Taconites (Michigan, Wisconsin, Minnesota)	51.5
8	South Africa	Sishen hematite	36.5
9	Canada	Labrador geosyncline (Wabush): Precambrian sedimentary deposits enriched by weathering (>60 wt.% Fe)	30.8
10	Venezuela	Imataca belt (Cerro Bolivar, El Pao, San Isidro); taconite type	20.9
11	Sweden	Northern Lapland (Kiruna, Malmberget); magnetite intrusion with apatite	20.3
12	Kazakhstan		15.4
13	Iran		12
14	Mexico		11
15	Mauritania	Zouerat	9.6
World total			1008

Sources: (i) Record trade in iron ore. *Min. J.* (London) no. 8744 July 11 (2003), pp. 21–23; (ii) *The Iron Ore Market 2002–2004*, UNCTAD Iron Ore Trust Fund, UNCTAD, Geneva, Switzerland (2003)

The world's eight largest iron ore producers (2002 annual production expressed in millions of tonnes) are listed in Table 2.6.

Table 2.6. Major iron ore producers (2002)

Company (Country)	Production (/10 ⁶ tonnes)
Companhia Vale do Rio Doce (CVRD) (Brazil)	163.6
Rio Tinto (UK/Australia)	93.8
BHP Billiton (UK/Australia)	80.8
State of India (India) (incl. SAIL, NMDC, Kudremukh)	38.6
Mitsui (Japan)	31.8
Kumba Resources (RSA)	18.6
Metalloinvest (Russia)	27.7
State of Ukraine (Ukraine) (incl. Ukrudprom)	20.5
State of Sweden (Sweden) (incl. LKAB)	20.3
Lebedinsky GOK (Russia)	18.4
State of Venezuela (Venezuela) (incl. CVG Ferrominera Orinoco)	16.5
USX (USA)	16.4
State of China (PRC) (incl. Anshan Iron & Steel)	14.9
Cleveland-Cliffs (USA)	14.4
Sokolovsky-Sarbaisky GPO (Kazakhstan)	13.1

Sources: (i) Record trade in iron ore. *Min. J.* (London) No. 8744 July 11 (2003), pp. 21–23; (ii) *The Iron Ore Market 2002–2004*, UNCTAD Iron Ore Trust Fund, UNCTAD, Geneva, Switzerland (2003)

Table 2.7. Top ten crude-steel-producing countries (2003)

Rank	Producing country	Production (/10 ⁶ tonnes)
1	China	220.1
2	Japan	110.5
3	United States	91.4
4	Russia	61.3
5	South Korea	46.3
6	Germany	44.8
7	Ukraine	36.7
8	India	31.8
9	Brazil	31.1
10	Italy	26.7
	Other	261.80
World total		962.5

In terms of crude steel production, according to the International Iron and Steel Institute (ISII), in 2003 the total world crude steel production reached 962.5 million tonnes, with 40% produced in Asia. The top ten crude-steel-producing countries are listed in Table 2.7.

2.1.6 Mining and Mineral Dressing

Most iron ores are mined by common open-pit techniques. Some underground mines exist, but, wherever possible, surface mining is preferred because it is less expensive. After mining, depending on the quality of the raw iron ore, two methods can be used to prepare the concentrated ore. Common ore is crushed and ground in order to release the ore minerals from the inert gangue materials (e.g., silica and silicates). Gangue minerals are separated from iron ore particles by common ore beneficiation processes in order to decrease silica content to less than 9 wt.%. Most concentration processes use froth flotation and gravity separation based on density differences to separate light gangue minerals from heavier iron ores. Electromagnetic separation techniques are also used, but hematite is not ferromagnetic enough to be easily recovered. After beneficiation, the iron ore concentrate is in the powdered form and, hence, unsuitable for use directly in the blast furnace. It has a much smaller particle size than ore fines and cannot be agglomerated by sintering. Instead, concentrates must be agglomerated by the process of **pelletizing** (which originated in Sweden and Germany in 1911 and was optimized in the 1940s). In this process, humidified concentrates are first fired into a rotary kiln in which the tumbling action produces soft, spherical agglomerates. These agglomerates are then dried and hardened by firing in air at a temperature ranging between 1250°C and 1340°C, yielding spherical pellets with about a 1-cm diameter. For certain rich iron ore deposits the raw ore (above 66 wt.% Fe) is crushed to reduce the maximum particle size and sorted into various fractions by passing it over sieves through which lump or rubble ore (i.e., 5 to 25 mm) is separated from the fines (i.e., less than 5 mm). Due to the high iron content, the lumps can be charged directly into the blast furnace without any further processing. Fines, however, must first be agglomerated, which means reforming them into lumps of suitable size by a process called **sintering**, an agglomeration process in which fines are

heated in order to achieve partial melting, during which ore particles fuse together. For this purpose, the elevated heat required is generated by burning the fine coke known as coke breeze. After cooling, the sinter is broken up and screened to yield blast-furnace feed and an undersize fraction that is recycled.

2.1.7 Iron- and Steelmaking

Highly pure iron is prepared on a small scale by the reduction of pure oxide or hydroxide with hydrogen, or by the carbonyl process in which iron is heated with carbon monoxide under pressure and the $\text{Fe}(\text{CO})_5$ so formed decomposed at 250°C to give off the powdered metal. By contrast, the industrial production of steel by the conversion of iron ore into steel in a blast furnace accounts for the largest tonnage of any metal produced by humans. Actually in 2005, 1.107×10^9 tonnes of crude steel were produced worldwide, with 62% produced by the oxygen steelmaking method, 34% by electric steelmaking, and the remaining 4% by smelting reduction. This amount of crude steel requires upstream ca. 1.292×10^9 tonnes of iron feedstocks, which breaks down as follows: 749 million tonnes (58%) of hot metal, 491 million tonnes (38 %) of reclaimed steel scrap, and finally 52 million tonnes (4%) of direct reduced iron.

The blast furnace. Ironmaking consists in winning iron metal from iron chemically combined with oxygen. The blast-furnace process, which consists in the carbothermic reduction of iron oxides, is industrially the most efficient process. From a chemical engineering point of view, the blast furnace can be described as a countercurrent heat and oxygen exchanger in which rising combustion gas loses most of its heat on the way up, leaving the furnace at a temperature of about 200°C , while descending iron oxides are reduced to metallic iron. The **blast furnace** is a tall, vertical steel reactor lined internally with refractory ceramics such as high-alumina firebrick (45 to 63 wt.% Al_2O_3) and graphite. Five sections can be clearly identified:

- (i) At the bottom is a parallel-sided hearth where liquid metal and slag collect. This is surmounted by
- (ii) an inverted truncated cone known as the **bosh**. Air is blown into the furnace through
- (iii) **tuyeres**, i.e., water-cooled copper nozzles, mounted at the top of the hearth close to its junction with the bosh.
- (iv) A short vertical section called the bosh parallel, or the barrel, connects the bosh to the truncated upright cone that is the stack.
- (v) Finally, the fifth and top section, through which the charge is fed into the furnace, is the **throat**.

The lining in the bosh and hearth, where the highest temperatures occur, is usually made of carbon bricks, which are manufactured by pressing and baking a mixture of coke, anthracite, and pitch. Actually, carbon exhibits excellent corrosion resistance to molten iron and slag in comparison with the aluminosilicate firebricks used for the remainder of the lining.

During the blast-furnace process, the solid charge (i.e., mixture of iron ore, limestone, and coke) is loaded either by operated skips or by conveyor belts at the top of the furnace at temperatures ranging from 150 to 200°C , while preheated air (i.e., 900 to 1350°C) in hot-blast stoves, sometimes enriched up to 25 vol.% O, is blown into the furnace through the tuyeres. During the process, the coke serves both as fuel and reducing agent, and a fraction combines with iron. The limestone acts as a fluxing agent, i.e., it reacts with both silica gangue materials and traces of sulfur to form a slag. Sometimes fluorspar is also used as fluxing agent. During the carbothermic reduction, the ascending carbon monoxide (CO) resulting from the exothermic combustion of coke at the tuyere entrance begins to react with the descending

charge, partially reducing the ore to ferrous oxide (FeO). At the same time the CO is cooled by the descending charge and reacts, forming carbon dioxide (CO₂) and carbon black (soot). This soot is dissolved in the iron, forming a eutectic, and hence decreases the melting temperature. At this stage, the temperature is sufficiently high to decompose the limestone into lime (CaO) and CO₂. Carbon dioxide reacts with the coke to give off CO, and the free lime combines with silica gangue to form a molten silicate slag floating upon molten iron. Slag is removed from the furnace by the same taphole as the iron, and it exhibits the following chemical composition: 30 to 40 wt.% SiO₂, 5 to 15 wt.% Al₂O₃, 35 to 45 wt.% CaO, and 5 to 15 wt.% MgO. As the partially reduced ore descends, it encounters both increasingly high temperature and high concentration of CO, which accelerates the reactions. At this stage the reduction of ferrous oxide into iron is completed and the main product, called molten pig iron (i.e., hot metal or blast-furnace iron), is tapped from the bottom of the furnace at regular intervals. The gas exiting at the top of the furnace is composed mainly of 23 vol.% CO, 22 vol.% CO₂, 3 vol.% H₂O, and 49 vol.% N₂, and after the dust particles have been removed using dust collectors, it is mixed with coke oven gas and burned in hot-blast stoves to heat the air blown in through the tuyeres. It is important to note that during the process, traces of aluminum, manganese, and silicon from the gangue are oxidized and recovered into the slag, while phosphorus and sulfur dissolve into the molten iron.

Direct reduction iron. The blast-furnace process is strongly dependent on the commercial availability of coke. For that reason, numerous substitute processes have been investigated since the 1950s to produce a prereduced product for crude steelmaking based on iron ore reduction without using coke as a reductant and to avoid operation of a capital-intensive coke oven plant. These technologies have been especially attractive in countries suffering a coke supply deficit, and hence they are used in Central and South America, India, and Africa. These processes are grouped under the term *direct reduction* and *smelting reduction*. Direct reduction processes produce solid *direct reduced iron* (DRI) or *hot briquetted iron* (HBI), while smelting reduction processes produce *liquid hot metal*. However, despite their great promise, these technologies have never superseded the blast furnace, especially in industrialized countries, for the following reasons:

- (i) Direct reduction is attractive at locations where cheap energy and particularly cheap natural gas is available.
- (ii) The development of a market for steel scrap as a raw material acts against direct reduction. Direct reduction can be divided according to the type of reductant used (i.e., natural gas, coal) or the screen size of iron ore (i.e., coarse, fines).

Table 2.8. Processes for direct reduction

Gas reduction		Coal-based reduction	
Shaft furnace	Midrex	Rotary kiln	SL/RN
	HyL III	Fluidized bed	Circofer
	Arex	Rotary hearth	Inmetco
Retort	HyL I and II		Fastmet
Fluidized bed	Fior		Sidcomet
	Finmet		DRyrllon
	Iron Carbide	Multiple hearth furnace	Primus
	Circored		

Source: Steffen, R.; Längen, H.-B. State of the art technology of direct and smelting reduction of iron ores. *La Revue de Métallurgie*, No.3, March 2004, pp. 171–182

2.1.8 Pure Iron Grades

Table 2.9. Pure iron grades

Pure iron grade	Purity (/ wt.% Fe)	Description
Ingot iron	99.8–99.9	Ingot iron is a nearly chemically pure iron type (i.e., 99.8 to 99.9wt.%Fe) that is used for construction work where a ductile, rust-resistant metal is required. It is mainly applied for boilers, tanks, enamel ware, and galvanized culvert sheets, as well as for electromagnetic cores and as a raw material for producing specialty steels. A well-known commercial type is Armco ingot iron (99.94 wt.% Fe). Typical ingot irons have as little as 0.02 wt.% C or less. The Armco ingot iron, for example, typically has carbon concentrations of 0.013 wt.% C and a manganese content around 0.017 wt.% Mn. Ingot iron may also be obtained in grades containing 0.25 to 0.30 wt.% copper, which increases the corrosion resistance. Ingot iron is made by the basic open-hearth process and highly refined, remaining in the furnace 1 to 4 h longer than the normal time, and maintained at a temperature of 1600 to 1700°C.
Electrolytic iron	99.9	Electrolytic iron is a chemically pure iron (i.e., 99.9 wt.% Fe) produced by the cathodic deposition of iron in an electrochemical refining process. Bars of cast iron are used as consumable and soluble anodes and dissolved in an electrolyte bath containing iron (II) chloride (FeCl_2) with a current density ranging from 200 to 1000 A.m^{-2} at a pH close to 1.1 to prevent both hydrogen evolution that decreases faradaic efficiency and the precipitation of iron hydroxides. Due to the ease of stripping, the cathodic reduction of ferrous cations yields pure iron deposited onto titanium metal cathodes, which are often hollow cylinders. The deposited iron tube is removed by hydraulic pressure or by splitting and then annealed and rolled into plates. The product is used for magnetic cores and in general in applications where both elevated ductility and purity are required.
Pig iron	94.6	Pig iron is obtained from the smelting of hemo-ilmenite with anthracite coal in ac- or dc-electric arc furnaces. Pig iron with typically 4.25 wt.% C is commercialized under the tradename Soremetal and has been produced since 1950 by slagging at the metallurgical complex of QIT-Fer & Titane in Sorel-Tracy, Qc, Canada and later in the 1970s at Richards Bay Minerals, South Africa.
Reduced iron	99.9	Reduced iron is a fine gray amorphous powder made by reducing crushed iron ore by heating in hydrogen atmosphere. It is used for special chemical purposes.
Carbonyl iron	99.99	Carbonyl iron or carbonyl iron powder is metallic iron of extreme purity, produced as microscopic spherical particles by the reaction of carbon monoxide on iron ore. This reaction gives a liquid, called iron carbonyl $\text{Fe}(\text{CO})_5$, that is vaporized and deposited as a powder. Carbonyl iron is mainly used for magnetic cores for high-frequency equipment and for pharmaceutical application of iron.
Wrought iron	99	Whrought iron, which is no longer commercially produced, is a relatively pure iron containing nonmetallic slag inclusions produced by a blast furnace. Modern wrought iron products are actually made of low-carbon steel.

2.1.9 The Iron-Carbon (Fe-C) and Iron-Cementite (Fe-Fe₃C) Systems

Because carbon is a ubiquitous element in both iron- and steelmaking processes due to its essential use as a reductant during the extractive process of iron from its ores, carbon has a predominant role in *siderurgy* (i.e., the metallurgy of iron and its alloys). Although other

alloying elements may be added to produce steels for special purposes, usually the structure of iron and steels is determined first by the content of carbon, secondly by the type of other alloying elements, and finally by the rate of cooling from the molten state. For all the above reasons, a solid grasp of the iron-carbon system is a mandatory step for understanding iron and iron alloys (i.e., steels and cast irons). As for the phase diagram of pure iron, the major phases occurring in the Fe-C phase diagram (Figure 2.1) can be accurately characterized by means of X-ray diffraction, thermal analysis, and dilatometry techniques. In practice, the iron-carbon phase diagram is a graphical plot of phases existing in thermodynamic equilibrium as a function of temperature versus the mass fraction of total carbon in the iron. The diagram depicted in this book is only a detail of the entire diagram. Actually, the phase diagram extends on the abscissa axis at left from pure iron free of carbon to a content of total carbon reaching 6.70 wt.% C that corresponds to the theoretical composition of iron carbide or cementite (Fe_3C), while temperatures range from 200°C to 1600°C, the temperature at

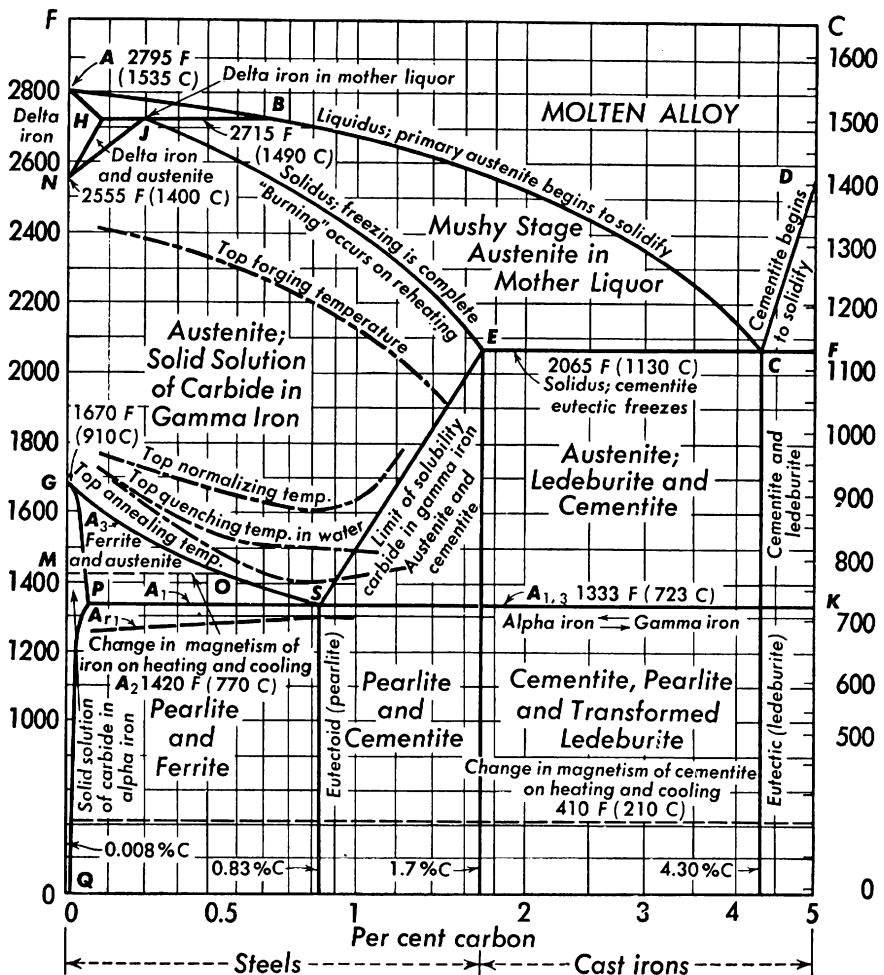


Figure 2.1. Simplified iron-carbon phase diagram. Source: Simplified iron-carbon phase diagram. *Metal Prog.*, vol. 52. Copyright © 1947 ASM International (reprinted with permission)

which the system is fully liquid. The binary phase diagram exhibits, in addition to the four critical points of the allotropes of pure iron, three other important characteristics:

- (i) a eutectic point at 4.30 wt.% C and 1148°C;
- (ii) a eutectoid point at 0.77 wt.% C and 727°C;
- (iii) a peritectic transformation occurring at 1495°C.

Moreover, experimentally the following solid phases were identified.

Alpha-ferrite (α -ferrite, bcc). *Sensu stricto* and historically, ferrite consists of a solid solution of carbon inside a body-centered cubic crystal lattice in alpha-iron. As mentioned in Section 2.1.2, the solubility of carbon in alpha-iron is extremely low, ca. 0.01 wt.% C at ambient temperature, and reaches only 0.025 wt.% C at 723°C. Therefore, at room temperature under conditions of equilibrium, any carbon present in excess of that small amount will exsolve in the form of cementite. Due to this low carbon content, some textbooks treat the ferrite phase substantially as pure iron, but this view must be discontinued to avoid confusion. Usually, the ferrite of an alloyed steel may contain in solid solution appreciable amounts of other elements; *ab extenso*, any solid solution of which alpha-iron is the solvent is called ferrite (i.e., a solid solution of any element in alpha-iron). Alloying elements that stabilize ferrite are listed in Table 2.11.

Beta-ferrite (β -ferrite, bcc). Like alpha-ferrite, beta-ferrite consists of a solid solution of any element in body-centered cubic beta iron.

Delta-ferrite (δ -ferrite, bcc). Like alpha-ferrite, delta-ferrite consists of a solid solution of any element in body-centered cubic delta iron. In the case of carbon, its maximum solubility in delta-iron is only 0.1 wt.% at 1487°C.

Gamma-austenite (γ -austenite, fcc). Austenite is a solid insertion solution of carbon into the crystal lattice of face-centered cubic gamma-iron. It has been definitively established that the carbon atoms in austenite occupy interstitial positions in the face-centered cubic space lattice causing the lattice parameter to increase progressively with the carbon content.

Cementite. Cementite is an iron carbide with the chemical formula Fe_3C . At room temperature, cementite is a hard, brittle, and ferromagnetic material with a Curie temperature of 210°C. It is formed by chemical reaction between iron and excess carbon. Three distinct origins must, however, be distinguished:

- (i) primary cementite resulting from the separation during solidification of liquid iron with carbon content ranging between 4.3 wt.% and 6.69 wt.% C;
- (ii) secondary cementite formed after demixion of carbon as a result of a decrease in miscibility during the cooling of ferrite;
- (iii) tertiary cementite resulting from demixion during the cooling of austenite. Actually, at room temperature under conditions of equilibrium, any carbon present in excess of that small amount must exist in a form other than that of a solute in a solid solution.

Perlite. A biphasic eutectoidic constituent that consists of an interlamellar growth of ferrite and cementite. Perlite is formed during the transformation of austenite with a eutectoid composition (i.e., 0.77 wt.% C).

Ledeburite. A biphasic eutectic constituent resulting from the solidification of a molten metal having a eutectic composition. Hence it consists of an austenite containing 1.7 wt.% C in solid solution and cementite.

In the phase diagrams in Figures 2.1 and 2.2, the transition temperatures or *critical points* previously identified for the four iron allotropes must now be replaced by two temperature limits or points. Actually, due to hysteresis phenomena occurring upon heating and cooling, the equilibrium curves are greatly influenced by the rate of cooling and heating, and they form distinct plots. The various temperatures at which pauses occur in the rise or fall of temperatures when iron or steel is heated from room temperature or cooled from the molten

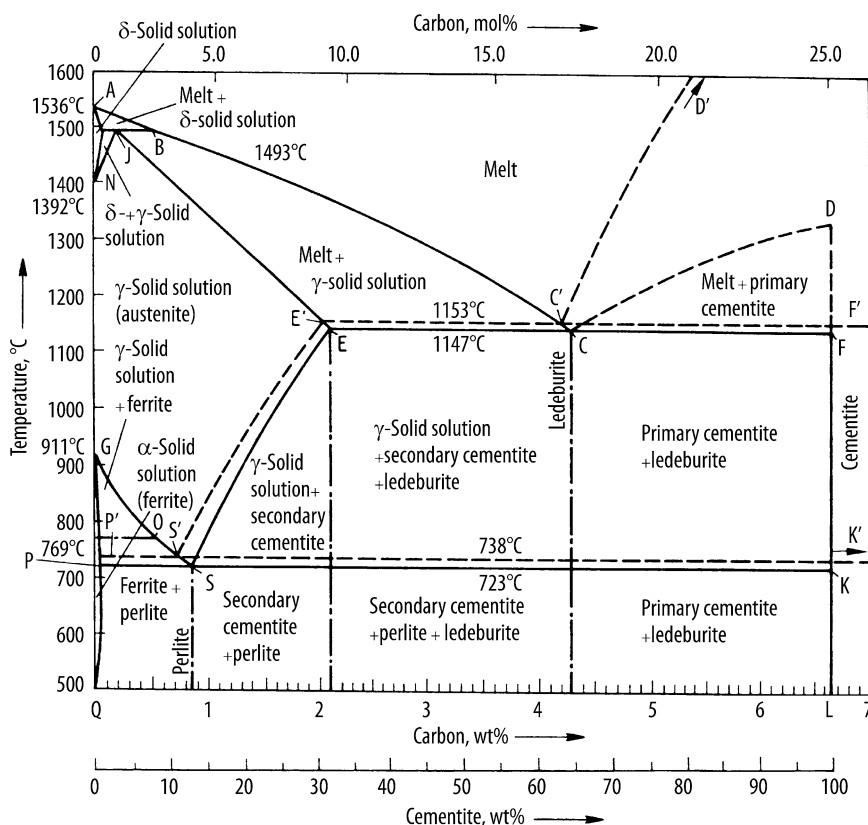


Figure 2.2. Detailed iron-cementite phase diagram. Source: *Ullmann's Encyclopedia of Industrial Chemistry*, 5th enhanced ed., vol. A14, p. 484, figure 11 in encyclopedia. Iron-cementite phase diagram. Copyright © 1989 Wiley-VCH (reproduced and redrawn with permission)

state are called **arrest points**, denoted by uppercase letter *A*. Due to the previously mentioned hysteresis behavior during heating and cooling, the arrest points obtained on heating are denoted A_c and those obtained on cooling are denoted A_r , while arrest points at equilibrium are denoted A_e . Historically, the subscripts *c*, *r*, and *e* were derived from the first letters of the French words *chauffage* (heating), *refroidissement* (cooling), and *équilibre* (equilibrium), respectively. These arrest points are described in detail in Table 2.10.

From the iron-carbon phase diagram several important characteristics regarding the classification of iron and iron alloys can be seen. Iron alloys are classified according to their total content of carbon. Steel are particular iron alloys having a carbon content below 2.1 wt.% C. Above this limit, we have cast irons up to a practical limit of 3.75 wt.% C. A steel containing 0.77 wt.% C is called a **eutectoid steel**. Eutectoid steel consists of an intimate mixture of alpha-ferrite and cementite forming an intergrowth of thin plates or lamellae known as **perlite**. Therefore, a steel having a carbon content below 0.77 wt.% C is called a **hypotectoid steel**. Its structure consists of a small amount of pearlite with an excess of alpha-ferrite, which collect at the grain boundaries. Hypotectoid steels are hence softer and more ductile than eutectoid steels. On the other hand, a steel with more than 0.77 wt.% C is called a **hypertectoid steel**. Its structure consists of pearlite with an excess of cementite. Hypertectoid steels are harder, more brittle, and less ductile than eutectoid steels. Above 2.11 wt.% C, molten iron solidifies

Table 2.10. Critical arrest points in iron-carbon phase diagram

Point	Description
A ₀	The first critical point; occurs at 210°C, the temperature at which cementite loses its ferromagnetism (Curie point). This arrest point exhibits the same temperature either on heating or on cooling, and it has little importance in both iron- and steelmaking.
A ₁	Temperature at which the transformation between austenite and perlite occurs (738°C). Austenite forms upon heating or decomposes upon cooling into a lamellar eutectoid made of alpha-ferrite plus cementite according to $\gamma\text{-(Fe,C)} \rightarrow \alpha\text{-(Fe,C)} + \text{Fe}_3\text{C}$.
A _{e1}	Temperature of equilibrium.
A _{c1}	Temperature at which austenite with eutectoid composition forms upon heating (formerly called <i>decalescence point</i>).
A _{r1}	Temperature at which the transformation austenite with eutectoid composition transforms into ferrite and cementite upon cooling (formerly called <i>recalcescence point</i>). The latent heat released during transformation is so high that the steel can be seen to redden with a distinct sound.
A ₂	Temperature at which the transformation from austenite into perlite occurs (768°C). Austenite forms upon heating or decomposes upon cooling into a lamellar eutectoid made of beta-ferrite plus cementite according to $\gamma\text{-(Fe,C)} \rightarrow \beta\text{-(Fe,C)} + \text{Fe}_3\text{C}$.
A _{e2}	Temperature of equilibrium of transformation.
A _{c2}	Temperature at which austenite with eutectoid composition forms upon heating.
A _{r2}	Temperature at which the transformation austenite with eutectoid composition transforms into paramagnetic beta-ferrite and cementite upon cooling.
A ₃	Temperature at which austenite and alpha-ferrite coexist temporarily and above which only austenite exists.
A _{e3}	Temperature of equilibrium of transformation.
A _{c3}	Temperature at which the transformation alpha-ferrite-austenite is completed upon heating.
A _{r3}	Temperature at which the transformation of austenite into alpha-ferrite initiates upon cooling.
A ₄	Temperature at which austenite and beta-ferrite coexist temporarily and above which only austenite exists.
A _{e4}	Temperature of equilibrium of transformation.
A _{c4}	Temperature at which the transformation beta-ferrite-austenite is completed upon heating.
A _{r4}	Temperature at which the transformation of austenite into beta-ferrite initiates upon cooling.
A _{cm}	Temperature at which austenite and cementite coexist for steel with hypereutectoid composition and above which only austenite exists and below which only cementite exists.
A _{e cm}	Temperature of equilibrium of transformation.
A _{c cm}	Temperature at which the dissolution of cementite in austenite is completed upon heating.
A _{r cm}	Temperature at which the segregation of cementite from austenite initiates upon cooling.

always below 1350°C and the resulting low liquidus temperature iron alloys are called cast irons due to their ease of melting. The eutectic point in the Fe-C diagram is located at 4.3 wt.% C. At this composition, when the alloy solidifies, it forms a mixture of austenite with 1.7 wt.% C in solid solution and cementite; this eutectic structure is called ledeburite. In practice, cast irons exhibit a carbon content ranging between 2.11 and 3.75 wt.%. Upon cooling, cast irons exhibit a mixture of pearlite and cementite.

The iron-carbon phase diagram only applies to alloys that contain only iron and carbon. But because other desired or undesired alloying elements are usually originally present from

Table 2.11. Ferrite- and austenite-stabilizing elements

Effect	Alloying elements or impurities	Effect
Ferrite stabilizers (alphagenous)	Cr, Si, Al, Mo, W, Ti, V	Favor the existence of alpha-ferrite.
	B, S, Zr, Nb, Ce, Ta	Restrict domain of austenite.
Austenite stabilizers (gammagenous)	C, N, Cu	Enlarge domain of existence of austenite.
	Ni, Mn, Co	Allow the existence of the austenite structure even at room temperature.

the ironmaking process (e.g., O, C, Si, P, Mn, V) or are added intentionally (e.g., Ni, Cr, Mo), during steelmaking the iron-carbon phase diagram cannot show accurately the conditions that apply to actual steels. Hence it has to be modified appropriately to take into account the effect of the elements. These additional elements impact both the arrest points and equilibrium lines, and they also determine the existence or not of certain phases. Alloying elements with their related impact on iron-carbon phases are listed in Table 2.11.

2.1.10 Cast Irons

Cast irons contain much higher carbon and silicon levels than steels, theoretically higher than 1.8 wt.% but typically 3 to 5 wt.% Fe and 1 to 3 wt.% Si. These comprise another category of ferrous materials that are intended to be cast from the liquid state to the final desired shape. Various types of cast irons are widely used in industry, especially for valves, pumps, pipes, filters, and certain mechanical parts. Cast iron can be considered a ternary Fe-Si-C alloy. The carbon concentration is between 1.7 and 4.5%, most of which is present in insoluble form (e.g., graphite flakes or nodules). Such material is, however, normally called unalloyed cast iron and exists in four main types:

- (i) white iron, which is brittle and glass hard;
- (ii) unalloyed gray iron, which is soft but still brittle and which is the most common form of unalloyed cast iron;
- (iii) the more ductile malleable iron;
- (iv) nodular or ductile cast iron, the best modern form of cast iron, which has superior mechanical properties and equivalent corrosion resistance.

In addition, there are a number of alloy cast irons, many of which have improved corrosion resistance and substantially modified mechanical and physical properties. Generally, cast iron is not a particularly strong or tough structural material. Nevertheless, it is one of the most economical and is widely used in industry. Its annual production is surpassed only by steel. Iron castings are used in many items of equipment in the chemical-process industry, but its main use is in mechanical engineering applications: automobile and machine tools. Some of the best known classes, listed below, include the high-silicon and nickel cast irons.

- gray cast iron
- white cast iron
- chilled iron (duplex)
- malleable cast irons
- ductile or nodular cast irons

- alloy cast irons
- high-silicon cast irons
- nickel cast irons

2.1.10.1 Gray Cast Iron or Graphitic Iron

Gray cast irons contain 1.7 to 4.5 wt.% of C and other alloying elements such as Si, Mn, and Fe. Due to the slow cooling rate during casting, the carbon is precipitated as thin flakes of graphite dispersed throughout the metal. Therefore, gray cast irons are relatively brittle. Gray cast iron is the least expensive material, is quite soft, has excellent machinability, and is easy to cast into intricate shapes. Various strengths are produced by varying the size, amount, and distribution of the graphite. For instance, ultimate tensile strength typically ranges from 155 to 400 MPa and the Vickers hardness from 130 to 300 HV. Gray iron has excellent wear resistance and damping properties. However, it is both thermal and mechanical shock sensitive. Gray iron castings can be welded with proper techniques and adequate preheating of the components.

2.1.10.2 White Cast Iron

White cast iron is made by controlling the chemical composition (i.e., low Si, high Mn) and rate of solidification of the iron melt. Rapid cooling leads to an alloy that has practically all its carbon retained as dissolved cementite that is hard and devoid of ductility. The resulting cast is hard, brittle, and virtually unmachinable, and finishing must be achieved by grinding. Typically, the Vickers hardness ranges from 400 to 600 HV. Its main use is for wear- or abrasion-resistant applications. In this respect white irons are superior to manganese steel, unless deformation or shock resistance is required. The major applications of cast irons include pump impellers, slurry pumps, and crushing and grinding equipment.

2.1.10.3 Malleable Cast Irons

Malleable iron exhibits a typical carbon content of 2.5 wt.% C. It is made from white cast iron by prolonged heating of the casting. This causes the carbides to decompose, and graphite aggregates are produced in the form of dispersed compact rosettes (i.e., no flakes). This gives a tough, relatively ductile material. There are two main types of malleable iron, standard and pearlitic. The latter contains both combined carbon and graphite nodules. Standard malleable irons are easily machined. This is less so for pearlitic iron. All malleable cast irons withstand cold working and bending without cracking.

2.1.10.4 Ductile (Nodular) Cast Irons

This is the best modern form of cast iron as it has superior mechanical properties and equivalent corrosion resistance. Ductility is much improved and may approach that of steel. Ductile iron is sometimes also called nodular cast iron or spheroidal graphite cast iron, as the graphite particles are approximately spherical in shape, in contrast to the graphite flakes in gray cast iron. Ductile cast iron exhibits a typical microstructure. This is achieved by the addition of a small amount of nickel-magnesium alloy or by inoculating the molten metal with magnesium or cerium. Furthermore, composition is about the same as gray iron, with some nickel, and with more carbon (3.7 wt.% C) than malleable iron. There are a number of grades of ductile iron. Some have maximum machinability and toughness, others have maximum oxidation resistance. Ductile iron castings can also be produced to have improved low-temperature impact properties. This is achieved by adequate thermal treatment, by control of the phosphorus and silicon content, and by various alloying processes.

2.1.10.5 High-Silicon Cast Irons

Cast irons with a high silicon level (i.e., 13 to 16 wt.% Si), which are called Duriron, exhibit, for all concentrations of H_2SO_4 , even up to the boiling point, a constant corrosion rate of 130 $\mu\text{m}/\text{year}$ (i.e., 5 mpy). For these reasons, it is widely used in sulfuric acid service. Duriron is a cheap material that does not contain any amount of strategic metal. Nevertheless, it is very hard and brittle and thermal shock sensitive, so it is not readily machined or welded.

Table 2.12. Classification of cast irons⁴

Cast iron class	Average chemical composition range	Carbon-rich phase	Matrix	Fracture
Gray cast iron (FG) (flake graphite cast iron)	2.5–4.0 wt.% C 1.0–3.0 wt.% Si 0.2–1.0 wt.% Mn 0.002–1.0 wt.% P 0.02–0.25 wt.% S	Lamellar graphite	Pearlite	Gray
Compacted graphite cast iron (CG)	2.5–4.0 wt.% C 1.0–3.0 wt.% Si 0.2–1.0 wt.% Mn 0.01–0.1 wt.% P 0.01–0.03 wt.% S	Compacted vermicular graphite	Ferrite, pearlite	Gray
Ductile cast iron (SG) (nodular or spheroidal graphite cast iron)	3.0–4.0 wt.% C 1.8–2.8 wt.% Si 0.1–1.0 wt.% Mn 0.01–0.1 wt.% P 0.01–0.03 wt.% S	Spheroidal graphite	Ferrite, pearlite, austenite	Silver gray
White cast iron	1.8–3.6 wt.% C 0.5–1.9 wt.% Si 0.25–0.8 wt.% Mn 0.06–0.2 wt.% P 0.06–0.2 wt.% S	Cementite Fe_3C	Pearlite, martensite	White
Malleable cast iron (TG)	2.2–2.9 wt.% C 0.9–1.9 wt.% Si 0.15–1.2 wt.% Mn 0.02–0.2 wt.% P 0.02–0.2 wt.% S	Temper graphite	Ferrite, pearlite	Silver-gray
Mottled cast iron		Lamellar Graphite and cementite Fe_3C	Pearlite	Mottled
Austempered ductile iron		Spheroidal graphite	Bainite	Silver-gray

Note: Type of graphite flakes in gray cast iron: (A) uniform distribution, random orientation; (B) rosette grouping, random orientation; (C) superimposed flake size, random orientation; (D) interdendritic segregation, random orientation; (E) interdendritic segregation, preferred orientation.

⁴ from Stefanescu, D.M. (1992) *Classification and Basic Metallurgy of Cast Irons*. In: *ASM Metals Handbook*, vol. 1: *Ferrous Metals*. ASM, Metal Park, OH p. 3.

Table 2.13. Physical properties of gray cast irons

Type of Iron	Grade	Density ($\rho/\text{kg.m}^{-3}$)	Young's modulus (E/GPa)	Shear modulus (G/GPa)	Tensile strength (MPa)	Shear strength (MPa)	Compressive strength (MPa)	Brinell hardness (HB)	Coefficient linear thermal expansion ($/10^{-6}\text{K}^{-1}$)	Thermal conductivity ($\text{k/W.m}^{-1}.\text{K}^{-1}$)
Gray cast iron (FG) (flake graphite cast iron)	20	7200–7600	66–97	27–39	152	179	572	156	13	46–49
	25	7200–7600	79–102	32–41	179	220	669	174	13	46–49
	30	7200–7600	90–113	36–45	214	276	752	210	13	46–49
	35 (coarse pearlite)	7200–7600	100–119	40–48	252	334	855	212	13	46–49
	40 (fine pearlite)	7200–7600	110–138	44–54	293	393	965	235	13	46–49
	50 (acicular iron)	7200–7600	130–157	50–55	362	503	1130	262	13	46–49
	60	7200–7600	141–162	54–59	431	610	1293	302	13	46–49

Table 2.14. Physical properties of nodular and other cast irons										
Type of iron	Grade	Density ($\rho/\text{kg.m}^{-3}$)	Young's modulus (E/GPa)	Shear modulus (G/GPa)	Yield strength 0.2% proof (/MPa)	Ultimate tensile strength (/MPa)	Elongation (Z/%)	Brinell hardness (HB)	Coefficient linear thermal expansion (/ 10^{-6}K^{-1})	Thermal conductivity ($k/\text{W.m}^{-1}.\text{K}^{-1}$)
Ductile cast iron (SG) (nodular or spheroidal graphite cast iron)	60-40-18	7200-7600	169-172	66-69	190-220	300-350	22	150	12	35
	80-60-03	7200-7600	169-172	66-69	190-220	300-350	18	160	12	35
	60-40-18	7200-7600	169-172	66-69	200-250	300-410	18	180	12	35
	65-45-12	7200-7600	169-172	66-69	270-332	420-464	12	212	12	35
	80-55-06	7200-7600	169-172	66-69	320-362	450-559	11	221	12	35
	100-70-03	7200-7600	169-172	66-69	320	500	7	241	12	35
	120-90-02	7200-7600	169-172	66-69	370-864	600-974	1-3	269	12	35
	D4018	7200-7600	169-172	66-69	420	700	3	302	12	35
Compacted graphite cast iron (CG)	D4512	7200-7600	169-172	66-69	480	800		352	12	35
	D5506	7200-7600	169-172	66-69	600	900		359	12	35
	Ferritic	7200-7600	162	68	290	365	4.5	140-155	n.a.	41
	Pearlitic	7200-7600	165	68	330	440	1.5	225-245	n.a.	41
Malleable cast iron (TG)	A602	7200-7600	168	67.5	180	300	6	150	n.a.	n.a.
	A603	7200-7600	168	67.5	190	320	10	150	n.a.	n.a.
	A604	7200-7600	168	67.5	230-280	400-480	12	150	n.a.	n.a.

Table 2.15. Properties of alloyed cast irons

Alloyed cast iron class	Alloyed cast iron type	Density ($\rho/\text{kg.m}^{-3}$)	Ultimate tensile strength ($\sigma_{\text{UTS}}/\text{MPa}$)	Compressive strength (σ/MPa)	Brinell hardness (/HB)	Coefficient linear thermal expansion ($\alpha/10^{-6}\text{K}^{-1}$)	Thermal conductivity ($k/\text{W.m}^{-1}.\text{K}^{-1}$)	Electrical resistivity ($\rho/\mu\Omega.\text{cm}$)
Abrasion-resistant white iron	Low-carbon white iron	7600–7800	n.a.	n.a.	n.a.	12	22	53
	Martensitic nickel Cr iron	7600–7800	n.a.	n.a.	n.a.	8–9	30	80
Corrosion-resistant irons	High-silicon iron (Duriron®)	7000–7050	90–180	690	480–520	12.4–13.1	n.a.	50
	High-chromium iron	7300–7500	205–380	690	250–740	9.4–9.9	n.a.	n.a.
	High-nickel gray iron	7400–7600	170–310	690–1100	120–250	8.1–19.3	38–40	100
	High-nickel ductile	7400	380–480	1240–1380	130–240	12.6–18.7	13.4	78
Heat-resistant gray iron	Medium-silicon iron	6800–7100	170–310	620–1040	170–250	10.8	37	210
	High-nickel iron	7300–7500	170–310	690–1100	130–250	8.1–19.3	37–40	140–170
	Nickel-chromium-Si iron	7330–7450	140–310	480–690	110–210	12.6–16.2	30	150–170
	High-aluminum iron	5500–6400	180–350	n.a.	180–350	15.3	n.a.	n.a.
Heat-resistant white iron	High-chromium iron	7300–7500	210–620	690	250–500	9.3–9.9	20	120
Heat-resistant ductile iron	Medium-silicon ductile iron	7100	n.a.	n.a.	140–400	10.8–13.5	n.a.	58–87
	High-Ni ductile (20 wt.% Ni)	7400	380–415	1240–1380	140–200	18.7	13	77
	High-Ni ductile (23 wt.% Ni)	7400	400–450	n.a.	130–170	18.4	n.a.	100
	High-Ni ductile (30 wt.% Ni)	7500	n.a.	n.a.	n.a.	12.6–14.4	n.a.	n.a.
	High-Ni ductile (36 wt.% Ni)	7700	n.a.	n.a.	n.a.	7.2	n.a.	n.a.

2.1.11 Carbon Steels (C-Mn Steels)

Iron containing more than 0.15 wt.% C chemically combined is normally termed *steel*. This 0.15 wt.% C is a somewhat arbitrarily chosen borderline, and sometimes the nearly chemically pure “ingot iron” is referred to as *mild steel*. To make it even more confusing, the term

Table 2.16. Carbon- and low-alloy steel designation (AISI-SAE)

Series	Main group	Subgroups
1XXX	(Plain) carbon steel	10XX: Plain carbon (1.00 wt.% Mn, max) 11XX: Resulfurized 12XX: Resulfurized and rephosphorized 13XX: Manganese steels (1.75 wt.% Mn) 15XX: Nonresulfurized (1.00–1.65 wt.% Mn max)
2XXX	Nickel steels	23XX: 3.5 wt.% Ni 25XX: 5.0 wt.% Ni
3XXX	Nickel-chromium steels	31XX: 1.25 wt.% Ni and 0.65 to 0.80 wt.% Cr 32XX: 1.75 wt.% Ni and 1.07 wt.% Cr 33XX: 3.50 wt.% Ni and 1.50 to 1.57 wt.% Cr 34XX: 3.00 wt.% Ni and 0.77 wt.% Cr
4XXX	Molybdenum steels	40XX: 0.20 to 0.25 wt.% Mo 44XX: 0.40 to 0.52 wt.% Mo
	Chromium-molybdenum steels	41XX: 0.50 to 0.95 wt.% Cr, 0.12 to 0.30 wt.% Mo
4XXX	Nickel-molybdenum steels	46XX: 0.85–1.82 wt.% Ni, and 0.20–0.25 wt.% Mo 48XX: 3.50 wt.% Ni, 0.25 wt.% Mo
4XXX, 8XXX, 9XXX	Nickel-chromium-molybdenum steels	43XX: 1.82 wt.% Ni, 0.50 to 0.80 wt.% Cr, and 0.25 wt.% Mo 43BVXX: 1.82 wt.% Ni, 0.50 wt.% Cr, and 0.12–0.25 wt.% Mo 47XX: 1.05 wt.% Ni, 0.45 wt.% Cr, and 0.20 to 0.35 wt.% Mo, 0.03 wt.% V 81XX: 0.30 wt.% Ni, 0.40 wt.% Cr, and 0.12 wt.% Mo 86XX: 0.55 wt.% Ni, 0.50 wt.% Cr, and 0.20 wt.% Mo 87XX: 0.55 wt.% Ni, 0.50 wt.% Cr, and 0.25 wt.% Mo 88XX: 0.55 wt.% Ni, 0.50 wt.% Cr, and 0.35 wt.% Mo 93XX: 3.25 wt.% Ni, 1.20 wt.% Cr, and 0.12 wt.% Mo 94XX: 0.45 wt.% Ni, 0.40 wt.% Cr, and 0.12 wt.% Mo 97XX: 0.55 wt.% Ni, 0.20 wt.% Cr, and 0.20 wt.% Mo 98XX: 1.00 wt.% Ni, 0.80 wt.% Cr, and 0.25 wt.% Mo
5XXX	Chromium steels	50XX: 0.25 to 0.65 wt.% Cr 51XX: 0.80 to 1.05 wt.% Cr 50XXX: 0.50 wt.% Cr, min. 1 wt.% C 51XXX: 1.02 wt.% Cr, min. 1 wt.% C 52XXX: 1.45 wt.% Cr, min. 1 wt.% C
6XXX	Chromium-vanadium steels	61XX: 0.6 to 0.95 wt.% Cr, 0.10 to 0.15 wt.% V
7XXX	Tungsten-chromium steels	72XX: 1.75W, and 0.75Cr
9XXX	Silicon-manganese steels	92XX: 1.40 to 2.00 wt.% Si, 0.65 to 0.85 wt.% Mn, and 0.65 wt.% Cr

NB: The letter L, inserted between the second and third digits of the AISI or SAE number (e.g., 12L15 and 10L45), indicates a leaded steel, while standard killed carbon steels, which are generally fine-grained, may be produced with a boron treatment addition to improve hardenability. Such boron steels are produced within a range of 0.0005 to 0.0030 wt.% B and are identified by inserting the letter B between the second and third digits of the AISI or SAE number (e.g., 10B46).

mild steel is often also used as a synonym for **low-carbon steels** (see below), which are materials with 0.15 to 0.30 wt.% C. Steels that have been worked or wrought while hot are covered with a black scale, also called a **mill scale** made of magnetite (Fe_3O_4), and are sometimes called **black iron**. Cold-rolled steels have a bright surface, accurate cross section, and higher tensile and yield strengths. They are preferred for bar stock to be used for machining rods and for shafts. Carbon steels may be specified by chemical composition, mechanical properties, method of deoxidation, or thermal treatment and the resulting microstructure. However, wrought steels are most often specified by their chemical composition. No single element determines the characteristics of a steel; rather, the combined effects of several elements influence hardness, machinability, corrosion resistance, tensile strength, deoxidation of the solidifying metal, and the microstructure of the solidified metal. Standard wrought-steel compositions for both carbon and alloy steels are designated by the SAE-AISI four-digit code, the last two digits of which indicate the nominal carbon content (Table 2.16).

2.1.11.1 Plain Carbon Steels

Carbon steels, also called **plain carbon steels**, are primarily Fe and C, with small amounts of Mn. Specific heat treatments and slight variations in composition will lead to steels with varying mechanical properties. Carbon is the principal hardening and strengthening element in steel. Actually, carbon increases hardness and strength and decreases weldability and ductility. For plain carbon steels, about 0.20 to 0.25 wt.% C provides the best machinability. Above and below this level, machinability is generally lower for hot-rolled steels. Plain carbon steels are usually divided into three groups:

- (i) **Low-carbon steels** (e.g., AISI-SAE grades 1005 to 1030), or **mild steels**, contain up to 0.30 wt.% carbon. They are characterized by a low tensile strength and a high ductility. They are nonhardenable by heat treatment, except by surface hardening processes.
- (ii) **Medium-carbon steels** (e.g., AISI-SAE grades 1030 to 1055) have between 0.31 wt.% and 0.55 wt.% C. They provide a good balance between strength and ductility. They are hardenable by heat treatment, but hardenability is limited to thin sections or to the thin outer layer on thick parts.
- (iii) **High-carbon steels** (e.g., AISI-SAE grades 1060 to 1095) have between 0.56 wt.% and about 1.0 wt.% C. They are, of course, hardenable and are very suitable for wear-resistant and/or high-strength parts.

Low-carbon or mild steels. The lowest carbon group consists of the four AISI-SAE grades 1006, 1008, 1010, and 1015. All these grades consist of very pure iron with less than 0.30 wt.% C having a ferritic structure, and they exhibit the lowest carbon content of the plain carbon group. These steels exhibit a relatively low ultimate tensile strength and are not suitable for mechanically demanding applications. Both tensile strength and hardness rise with increases in carbon content and/or cold work, but such increases in strength are at the expense of ductility or the ability to withstand cold deformation. Hence mild steels are selected when cold formability is required. They are produced both as rimmed and killed steels. **Rimmed steels** are used for sheet, strip, rod, and wire where excellent surface finish or good drawing qualities are required, such as oil pans and other deep-drawn and formed products. Rimmed steels are also used for cold-heading wire for tacks, and rivets and low-carbon wire products. **Aluminum-killed steels** (i.e., AK steels) are used for difficult stampings or where nonaging properties are needed. **Silicon-killed steels** (i.e., SK steels) are preferred to rimmed steels for forging or heat-treating applications. With less than 0.15 wt.% C, the steels are susceptible to serious grain growth, causing brittleness, which may occur as the result of a combination of critical strain from cold work followed by heating to elevated temperatures. Steels in this group due to their ferritic structure do not machine freely and should be avoided for

cut screws and operations requiring broaching or smooth finish on turning. The machinability of bar, rod, and wire products is improved by cold drawing. Mild steels are readily welded.

Carburizing steels. This second group consists of the 13 AISI-SAE grades 1016, 1017, 1018, 1019, 1020, 1021, 1022, 1023, 1024, 1025, 1026, 1027, and 1030. Because of their higher carbon content they exhibit enhanced tensile strength and hardness but at the expense of cold formability. For heat-treating purposes, they are known as *carburizing* or *case-hardening steels*. Killed steels are recommended for forgings, while for other uses semikilled or rimmed steel may be suitable. Rimmed steels can ordinarily be supplied with up to 0.25 wt.% C. Higher carbon content provides a greater core hardness with a given quench or permits the use of thicker sections. An increase in manganese improves the hardenability of both the core and the case along with machinability; in carbon steels this is the only change in composition that will increase case hardenability. For carburizing applications, grades AISI 1016, 1018, and 1019 are widely used for thin sections or water-quenched parts. AISI 1022 and 1024 are used for heavier sections or where oil quenching is desired, and AISI 1024 is sometimes used for such parts as transmission and rear axle gears. AISI 1027 is used for parts given a light case to obtain satisfactory core properties without drastic quenching. AISI 1025 and 1030, although not usually regarded as carburizing types, are sometimes used in this manner for larger sections or where greater core hardness is needed. For cold-formed or cold-headed parts, the lowest manganese grades (i.e., AISI 1017, 1020, and 1025) offer the best formability at their carbon level. AISI 1020 is used for fan blades and some frame members, and 1020 and 1025 are widely used for low-strength bolts. The next highest manganese types, i.e., AISI 1018, 1021, and 1026, provide increased strength. All carburizing steels can be readily welded or brazed.

Medium-carbon steels. This group consists of the 16 AISI-SAE grades 1030, 1033, 1034, 1035, 1036, 1038, 1039, 1040, 1041, 1042, 1043, 1045, 1046, 1049, 1050, and 1052 with a carbon content of between 0.31 and 0.55 wt.% C. They are usually selected for their higher mechanical properties and are frequently further hardened and strengthened by heat treatment or by cold work. They are usually produced as killed steels and are suitable for a wide variety of automotive-type applications. Increases in the mechanical properties required in section thickness or in depth of hardening ordinarily indicate either higher carbon or manganese content or both. The heat-treating practice preferred, particularly the quenching medium, has a great effect on the steel selected. In general, any of the grades over 0.30 wt.% C may be selectively hardened by induction heating or flame methods. The lower-carbon and manganese steels in this group find usage for certain types of cold-formed parts. AISI 1030 is used for shift and brake levers. AISI 1034 and 1035 are used in the form of wire and rod for cold upsetting such as bolts, and AISI 1038 for bolts and studs. The parts cold-formed from these steels are usually heat treated prior to use. Stampings are generally limited to flat parts or simple bends. The higher-carbon AISI 1038, 1040, and 1042 are frequently cold drawn to specified physical properties for use without heat treatment for some applications such as cylinder head studs. Any of this group of steels may be used for forgings, the selection being governed by the section size and the physical properties desired after heat treatment. Thus, AISI 1030 and 1035 are used for shifter forks and many small forgings where moderate properties are desired, but the deeper-hardening AISI 1036 is used for more critical parts where a higher strength level and more uniformity are essential, such as some front-suspension parts. Forgings such as connecting rods, steering arms, truck front axles, axle shafts, and tractor wheels are commonly made from the AISI 1038 to 1045 group. Larger forgings at similar strength levels need more carbon and perhaps more manganese; for instance, crankshafts are made from AISI 1046 and 1052. These steels are also used for small forgings where high hardness after oil quenching is desired. Suitable heat treatment is necessary on forgings from this group to provide machinability. It is also possible to weld these steels by most commercial methods, but precautions should be taken to avoid cracking from too rapid cooling.

High-carbon steels. These are the 14 AISI-SAE grades 1055, 1060, 1062, 1064, 1065, 1066, 1070, 1074, 1078, 1080, 1085, 1086, 1090, and 1095. These steels contain more carbon than is required to achieve maximum “as quenched” hardness. They are used for applications requiring improved wear resistance for cutting edges and to make springs. In general, cold forming cannot be used with these steels, and forming is only limited to flat stampings and springs coiled from small-diameter wire. Practically all parts from these steels are heat treated before use. Uses in the spring industry include AISI 1065 for pretempered wire and 1066 for cushion springs of hard-drawn wire; 1064 may be used for small washers and thin stamped parts, 1074 for light flat springs formed from annealed stock, and 1080 and 1085 for thicker flat springs. 1085 is also used for heavier coil springs. Finally, valve spring wire and music wire are special products.

Easily machinable carbon steels. The three AISI-SAE grades 1111, 1112, and 1113 are intended for applications where easy machining is the primary requirement. They are characterized by a higher sulfur content than comparable carbon steels, machinability improving within the group as sulfur increases but at the expense of cold-forming, weldability, and forging properties. In general, the uses are similar to those for carbon steels of similar carbon and manganese content. These steels are commonly known as Bessemer screw stock and are considered the best machining steels available. Although of excellent strength in the cold-drawn condition, they have an unfavorable property of cold shortness and are not commonly used for vital parts. These steels may be cyanided or carburized, but when uniform response to heat treating is necessary, open-hearth steels are recommended. The nine AISI-SAE grades 1109, 1114, 1115, 1116, 1117, 1118, 1119, 1120, and 1126 are used where a combination of good machinability and more uniform response to heat treatment is required. The lower-carbon varieties are used for small parts that are to be cyanided or carbonitrided. AISI 1116, 1117, 1118, and 1119 contain more manganese for better hardenability, permitting oil quenching after case-hardening heat treatments. The higher-carbon 1120 and 1126 provide more core hardness when this is needed. Finally, grades AISI-SAE 1132, 1137, 1138, 1140, 1141, 1144, 1145, 1146, and 1151 exhibit a composition similar to that of carbon steels of the same carbon level, except they have a higher sulfur content. They are widely used for parts where large amounts of machining are necessary or where threads, splines, or other contours present special problems with tooling. AISI 1137 is widely used for nuts and bolts. The higher-manganese grades 1132, 1137, 1141, and 1144 offer greater hardenability, the higher-carbon types being suitable for oil quenching for many parts. All these steels may be selectively hardened by induction or flame heating.

Table 2.17. Typical chemical composition of plain carbon steels (wt.%)

AISI-SAE	UNS	C	Mn	P _{max}	S _{max}
1005	G10050	0.06 max	0.35	0.040	0.050
1006	G10060	0.08 max	0.25–0.40	0.040	0.050
1008	G10080	0.10 max	0.30–0.50	0.040	0.050
1010	G10100	0.08–0.13	0.30–0.60	0.040	0.050
1012	G10120	0.10–0.15	0.30–0.60	0.040	0.050
1015	G10150	0.13–0.18	0.30–0.60	0.040	0.050
1016	G10160	0.13–0.18	0.60–0.90	0.040	0.050
1017	G10170	0.15–0.20	0.30–0.60	0.040	0.050
1018	G10180	0.15–0.20	0.60–0.90	0.040	0.050
1019	G10190	0.15–0.20	0.70–1.00	0.040	0.050

Table 2.17. (continued)

AISI-SAE	UNS	C	Mn	P _{max}	S _{max}
1020	G10200	0.18–0.23	0.30–0.60	0.040	0.050
1021	G10210	0.18–0.23	0.60–0.90	0.040	0.050
1022	G10220	0.18–0.23	0.70–1.00	0.040	0.050
1023	G10230	0.20–0.25	0.30–0.60	0.040	0.050
1025	G10250	0.22–0.28	0.30–0.60	0.040	0.050
1026	G10260	0.22–0.28	0.60–0.90	0.040	0.050
1029	G10290	0.25–0.31	0.60–0.90	0.040	0.050
1030	G10300	0.28–0.34	0.60–0.90	0.040	0.050
1035	G10350	0.32–0.38	0.60–0.90	0.040	0.050
1037	G10370	0.32–0.38	0.70–1.00	0.040	0.050
1038	G10380	0.35–0.42	0.60–0.90	0.040	0.050
1039	G10390	0.37–0.44	0.70–1.00	0.040	0.050
1040	G10400	0.37–0.44	0.60–0.90	0.040	0.050
1042	G10420	0.40–0.47	0.60–0.90	0.040	0.050
1043	G10430	0.40–0.47	0.70–1.00	0.040	0.050
1044	G10440	0.43–0.50	0.30–0.60	0.040	0.050
1045	G10450	0.43–0.50	0.60–0.90	0.040	0.050
1046	G10460	0.43–0.50	0.70–1.00	0.040	0.050
1049	G10490	0.46–0.53	0.60–0.90	0.040	0.050
1050	G10500	0.48–0.55	0.60–0.90	0.040	0.050
1053	G10530	0.48–0.55	0.70–1.00	0.040	0.050
1055	G10550	0.50–0.60	0.60–0.90	0.040	0.050
1059	G10590	0.55–0.65	0.50–0.80	0.040	0.050
1060	G10600	0.55–0.65	0.60–0.90	0.040	0.050
1064	G10640	0.60–0.70	0.50–0.80	0.040	0.050
1065	G10650	0.60–0.70	0.60–0.90	0.040	0.050
1069	G10690	0.65–0.75	0.40–0.70	0.040	0.050
1070	G10700	0.65–0.75	0.60–0.90	0.040	0.050
1078	G10780	0.72–0.85	0.30–0.60	0.040	0.050
1080	G10800	0.75–0.88	0.60–0.90	0.040	0.050
1084	G10840	0.80–0.93	0.60–0.90	0.040	0.050
1086	G10860	0.80–0.93	0.30–0.50	0.040	0.050
1090	G10900	0.85–0.98	0.60–0.90	0.040	0.050
1095	G10950	0.90–1.03	0.30–0.50	0.040	0.050
1110	G11100	0.08–0.13	0.30–0.60	0.040	0.08–0.13
1117	G11170	0.14–0.20	1.00–1.30	0.040	0.08–0.13
1118	G11180	0.14–0.20	1.30–1.60	0.040	0.08–0.13
1137	G11370	0.32–0.39	1.35–1.65	0.040	0.08–0.13
1139	G11390	0.35–0.43	1.35–1.65	0.040	0.13–0.20

Table 2.17. (continued)

AISI-SAE	UNS	C	Mn	P _{max}	S _{max}
1140	G11400	0.37–0.44	0.70–1.00	0.040	0.08–0.13
1141	G11410	0.37–0.45	1.35–1.65	0.040	0.08–0.13
1144	G11440	0.40–0.48	1.35–1.65	0.040	0.24–0.33
1146	G11460	0.42–0.49	0.70–1.00	0.040	0.08–0.13
1151	G11510	0.48–0.55	0.70–1.00	0.040	0.08–0.13
1211	G12110	0.13max	0.60–0.90	0.07–0.12	0.10–0.15
1212	G12120	0.13max	0.70–1.00	0.07–0.12	0.16–0.23
1213	G12130	0.13max	0.70–1.00	0.07–0.12	0.24–0.33
1215	G12150	0.09max	0.75–1.05	0.04–0.09	0.26–0.35
1513	G15130	0.10–0.16	1.10–1.40	0.040	0.050
1522	G15220	0.18–0.24	1.10–1.40	0.040	0.050
1524	G15240	0.19–0.25	1.35–1.65	0.040	0.050
1526	G15260	0.22–0.29	1.10–1.40	0.040	0.050
1527	G15270	0.22–0.29	1.20–1.50	0.040	0.050
1541	G15410	0.36–0.44	1.35–1.65	0.040	0.050
1548	G15480	0.44–0.52	1.10–1.40	0.040	0.050
1551	G15510	0.45–0.56	0.85–1.15	0.040	0.050
1552	G15520	0.47–0.55	1.20–1.50	0.040	0.050
1561	G15610	0.55–0.65	0.75–1.05	0.040	0.050
1566	G15660	0.60–0.71	0.85–1.15	0.040	0.050
12L14(*)	G12144	0.15max	0.85–1.15	0.04–0.09	0.26–0.35
(*) 0.15–0.35 wt.% Pb.					

2.1.11.2 Low-Alloy Steels

Steels that contain specified amounts of alloying elements other than carbon and the commonly accepted amounts of manganese, copper, silicon, sulfur, and phosphorus are known as alloy steels. Alloying elements are added to change mechanical or physical properties. A steel is considered to be an alloy when the maximum of the range given for the content of alloying elements exceeds one or more of these limits: 1.65 wt.% Mn, 0.60 wt.% Si, or 0.60 wt.% Cu, or when a definite range or minimum amount of any of the following elements is specified or required within the limits recognized for constructional alloy steels: aluminum, chromium (up to 3.99%), cobalt, columbium, molybdenum, nickel, titanium, tungsten, vanadium, zirconium, or other element added to obtain an alloying effect. According to the previous definition, strictly speaking, tool and stainless steels are also considered alloy steels. However, the term alloy steel is reserved for those steels that contain a minute amount of alloying elements and that usually depend on thermal treatment to develop specific properties. Subdivisions for most steels in this family include through-hardening grades, which are heat treated by quenching and tempering and are used when maximum hardness and strength must extend deep within a part, while carburizing grades are used where a tough core and relatively shallow, hard surface is needed. After a surface-hardening treatment such as carburizing or nitriding for nitriding alloys, these steels are suitable for parts that must withstand wear as well as high stresses. Cast steels are generally through-hardened, not surface treated. Carbon content and alloying elements influence the overall characteristics of

both types of alloy steels. Maximum attainable surface hardness depends primarily on the carbon content. Maximum hardness and strength in small sections increase as carbon content increases, up to about 0.7 wt. % C. However, carbon content greater than 0.3% can increase the possibility of cracking during quenching or welding. Alloying elements primarily influence hardenability. They also influence other mechanical and fabrication properties including toughness and machinability. Lead additions (i.e., 0.15 to 0.35 wt.% Pb) greatly improve the machinability of alloy steels by high-speed-tool steels. For machining with carbide tools, calcium-treated steels are reported to double or triple tool life in addition to improving surface finish. Alloy steels are often specified when high strength is needed in moderate to large sections. Whether tensile or yield strength is the basis of design, thermally treated alloy steels generally offer high strength-to-weight ratios. In general, the wear resistance can be improved by increasing the hardness of an alloy, by specifying an alloy with greater carbon content, or by using nitrided parts, which have better wear resistance than would be expected from the carbon content alone. Fully hardened and tempered, low-carbon (i.e., 0.10 to 0.30 wt.% C) alloy steels have a good combination of strength and toughness, at both room and low temperatures.

Carburizing alloyed steels. The properties of carburized and hardened cases depend on the carbon and alloy content, the structure of the case, and the degree and distribution of residual stresses. The carbon content of the case depends on the carburizing process and on the reactivity of iron and of the alloying elements to carburization. The original carbon content of the steel has little or no effect on the carbon content produced in the case; hence the last two digits in the AISI-SAE specification numbers are not meaningful as far as the case is concerned. The hardenability of the case, therefore, depends on the alloy content of the steel and the final carbon content produced by carburizing. With complete carbide solution, the effect of alloying elements on the hardenability of the case is about the same as the effect of these elements on the hardenability of the core. As an exception to this statement, any element that inhibits carburizing may reduce the hardenability of the case. Some elements that raise the hardenability of the core may tend to produce more retained austenite and consequently somewhat lower hardness in the case. Alloy steels are frequently used for case hardening because the required surface hardness can be obtained by moderate quenching speeds. Slower quenching may mean less distortion than would be encountered with water quenching. It is usually desirable to select a steel that will attain a minimum surface hardness of 58 or 60 HRC after carburizing and oil quenching. Where section sizes are large, a high-hardenability alloy steel may be necessary, whereas for medium and light sections, low-hardenability steels will suffice.

The **case-hardening** alloy steels may be divided into two classes: high- and medium-hardenability case steels.

High-hardenability case steels. The five AISI-SAE grades 2500, 3300, 4300, 4800, and 9300 are high-alloy steels; hence both the case and the core possess a high hardenability. They are used particularly for carburized parts with thick sections, such as pinions and heavy gears. Good case properties can be obtained by oil quenching. These steels are likely to have retained austenite in the case after carburizing and quenching, and hence refrigeration may be required.

Medium-hardenability case steels. The AISI-SAE grades 1300, 2300, 4000, 4100, 4600, 5100, 8600, and 8700 have medium hardenability, which means that their hardenability is intermediate between that of plain carbon steels and the higher-alloy carburizing steels discussed previously. In general, these steels can be used for average-size case-hardened automotive parts such as gears, pinions, and crankshafts. Satisfactory case hardness is usually produced by oil quenching. The core properties of case-hardened steels depend on both the carbon and alloy content of the steel. Each of the general types of alloy case-hardening steel is usually made with two or more carbon contents to permit different hardenability in the core. The most desirable hardness for the core depends on the design and the type of

Table 2.18. (continued)

AISI-SAE	UNS	C	Mn	Pmax	Smax	Si	Ni	Cr	Mo
5117	G51170	0.15–0.20	0.70–0.90	0.035	0.040	0.15–0.35	...	0.70–0.90	...
5120	G51200	0.17–0.22	0.70–0.90	0.035	0.040	0.15–0.35	...	0.70–0.90	...
5130	G51300	0.28–0.33	0.70–0.90	0.035	0.040	0.15–0.35	...	0.80–1.10	...
5132	G51320	0.30–0.35	0.60–0.80	0.035	0.040	0.15–0.35	...	0.75–1.00	...
5135	G51350	0.33–0.38	0.60–0.80	0.035	0.040	0.15–0.35	...	0.80–1.05	...
5140	G51400	0.38–0.43	0.70–0.90	0.035	0.040	0.15–0.35	...	0.70–0.90	...
5150	G51500	0.48–0.53	0.70–0.90	0.035	0.040	0.15–0.35	...	0.70–0.90	...
5155	G51550	0.51–0.59	0.70–0.90	0.035	0.040	0.15–0.35	...	0.70–0.90	...
5160	G51600	0.56–0.64	0.75–1.00	0.035	0.040	0.15–0.35	...	0.70–0.90	...
6118	G61180	0.16–0.21	0.50–0.70	0.035	0.040	0.15–0.35	...	0.50–0.70	0.10–0.15 V min
6150	G61500	0.48–0.53	0.70–0.90	0.035	0.040	0.15–0.35	...	0.80–1.10	0.15 V min
8615	G86150	0.13–0.18	0.70–0.90	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.15–0.25
8617	G86170	0.15–0.20	0.70–0.90	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.15–0.25
8620	G86200	0.18–0.23	0.70–0.90	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.15–0.25
8622	G86220	0.20–0.25	0.70–0.90	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.15–0.25
8625	G86250	0.23–0.28	0.70–0.90	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.15–0.25
8627	G86270	0.25–0.30	0.70–0.90	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.15–0.25
8630	G86300	0.28–0.33	0.70–0.90	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.15–0.25
8637	G86370	0.35–0.40	0.75–1.00	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.15–0.25
8640	G86400	0.38–0.43	0.75–1.00	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.15–0.25
8642	G86420	0.40–0.45	0.75–1.00	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.15–0.25
8645	G86450	0.43–0.48	0.75–1.00	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.15–0.25
8655	G86550	0.51–0.59	0.75–1.00	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.15–0.25
8720	G87200	0.18–0.23	0.70–0.90	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.20–0.30
8740	G87400	0.38–0.43	0.75–1.00	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.20–0.30
8822	G88220	0.20–0.25	0.75–1.00	0.035	0.040	0.15–0.35	0.40–0.70	0.40–0.60	0.30–0.40
9260	G92600	0.56–0.64	0.75–1.00	0.035	0.040	1.80–2.20
50B44	G50441	0.43–0.48	0.75–1.00	0.035	0.040	0.15–0.35	...	0.40–0.60	...
50B46	G50461	0.44–0.49	0.75–1.00	0.035	0.040	0.15–0.35	...	0.20–0.35	...
50B50	G50501	0.48–0.53	0.75–1.00	0.035	0.040	0.15–0.35	...	0.40–0.60	...
50B60	G50601	0.56–0.64	0.75–1.00	0.035	0.040	0.15–0.35	...	0.40–0.60	...
51B60	G51601	0.56–0.64	0.75–1.00	0.035	0.040	0.15–0.35	...	0.70–0.90	...
81B45	G81451	0.43–0.48	0.75–1.00	0.035	0.040	0.15–0.35	0.20–0.40	0.35–0.55	0.08–0.15
94B17	G94171	0.15–0.20	0.75–1.00	0.035	0.040	0.15–0.35	0.30–0.60	0.30–0.50	0.08–0.15
94B30	G94301	0.28–0.33	0.75–1.00	0.035	0.040	0.15–0.35	0.30–0.60	0.30–0.50	0.08–0.15
E4340c	G43406	0.38–0.43	0.65–0.85	0.025	0.025	0.15–0.35	1.65–2.00	0.70–0.90	0.20–0.30
E51100c	G51986	0.98–1.10	0.25–0.45	0.025	0.025	0.15–0.35	...	0.90–1.15	...
E52100c	G52986	0.98–1.10	0.25–0.45	0.025	0.025	0.15–0.35	...	1.30–1.60	...

Table 2.19. Physical properties of plain carbon steels and low-alloy steels

AISI type	UNS	Density ($\rho/\text{kg.m}^{-3}$)	Yield strength 0.2% proof ($\sigma_{0.2}/\text{MPa}$) ⁵	Ultimate tensile strength ($\sigma_{\text{UTS}}/\text{MPa}$)	Elongation (Z/%) ⁶	Brinell hardness (HB)	Izod impact strength (J) ⁷	Coeff. linear thermal exp. ($\alpha/10^{-6} \text{K}^{-1}$)	Thermal conductivity ($k/\text{W.m}^{-1}.\text{K}^{-1}$)	Specific heat capacity ($c_p/\text{J.kg}^{-1}.\text{K}^{-1}$) (50–100°C)	Electrical resistivity ($\rho/\mu\Omega.\text{cm}$)
1008	G10080	7750						12.6	59.5	481	14.2
1010	G10100	7750	n.a.	310	25	121	n.a.	12.2	n.a.	450	14.3
1015	G10150	7750	285–325	386–425	37–39	111–126	111–115	12.2	51.9	486	15.9
1020	G10200	7750	200–355	395–690	12–21	126–179	87–123	11.7	51.9	486	15.9
1022	G10220	7750	315–360	450–505	34–35	137–149	81–121				
1025	G10250	7750	215–415	430–770	11–20	n.a.	n.a.	12.0	51.9	486	15.9
1030	G10300	7750	230–415	460–775	10–20	126–207	69–94	11.7	51.9	486	16.6
1035	G10350	7750	280–480	490–775	9–18	179–229	n.a.	11.1	50.8	486	16.3
1040	G10400	7750	245–530	510–770	7–17	149–255	45–65	11.3	50.7	486	16.0
1045	G10450	7750	280–525	540–770	7–16	n.a.	n.a.	11.6	50.8	486	16.2
1050	G10500	7750	280–585	570–1000	8–14	187–229	18–31	11.1	51.2	486	16.3
1060	G10600	7750	370–485	625–815	17–23	179–241	11–18				
1090	G10800	7750	380–585	615–1015	12–25	174–293	7				
1095	G10950	7750	380–570	655–1015	9–13	192–293	3–5				
1117	G11170	7750	285–305	430–490	33	121–143	81–94				
1118	G11180	7750	285–315	450–525	32–35	131–149	103–109				
1137	G11370	7750	345–400	585–670	23–27	174–197	50–83	12.8	50.5	n.a.	17.0
1141	G11410	7750	340–495	540–850	7–20	152–255	11–53	12.6	50.5	461	17.0
1144	G11440	7750	345–420	585–705	21–25	167–212	43–65				
1151	G11510	7750						12.6	50.5	502	17.0
1330	G13300	7750						12.0	n.a.	n.a.	n.a.
1335	G13350	7750						12.2	n.a.	n.a.	n.a.
1340	G13400	7750	435–560	705–835	22–26	207–248	71–92				
1345	G13450	7750						12.0	n.a.	n.a.	n.a.
1522	G15220	7750						12.0	51.9	486	n.a.
2330	G23300	7750	689	841	19	248		10.9	n.a.	n.a.	n.a.
2515	G25150	7750	648	779	25	233		10.9	34.3	n.a.	n.a.
3120	G31200	7750						11.3	n.a.	n.a.	n.a.
3140	G31400	7750	420–600	690–890	20–25	197–262	34–40	11.3	n.a.	n.a.	n.a.
3150	G31500	7750	n.a.	n.a.	n.a.	n.a.		11.3	n.a.	n.a.	n.a.

⁵ Maximum values: as-rolled or normalized conditions; minimum values: annealed conditions.⁶ Minimum values: as-rolled or normalized conditions; maximum values: annealed conditions.⁷ Minimum values: as-rolled or normalized conditions; maximum values: annealed conditions.

Table 2.19. (continued)

AlSi type	UNS	Density ($\rho/\text{kg.m}^{-3}$)	Yield strength 0.2% proof ($\sigma_{0.2}/\text{MPa}$) ⁵	Ultimate tensile strength (σ_{UTS}/MPa)	Elongation (Z/%) ⁶	Brinell hardness (HB)	Izod impact strength (J) ⁷	Coeff. linear thermal exp. ($\alpha/10^{-6} \text{K}^{-1}$)	Thermal conductivity ($k/\text{W.m}^{-1}.\text{K}^{-1}$)	Specific heat capacity ($c_p/\text{J.kg}^{-1}.\text{K}^{-1}$) (50–100°C)	Electrical resistivity ($\rho/\mu\Omega.\text{cm}$)
4023	G40230	7750	586	827	20	255		11.7	n.a.	n.a.	n.a.
4042	G40420	7750	1448	1620	10	461		11.9	n.a.	n.a.	n.a.
4053	G40530	7750	1538	1724	12	495		n.a.	n.a.	n.a.	n.a.
4063	G40630	7750	1593	1855	8	534		n.a.	n.a.	n.a.	n.a.
4130	G41300	7750	360–1172	560–1379	16–28	156–375	62–87	12.2	42.7	477	22.3
4140	G41400	7750	1172	1379	15	385		12.3	42.7	475	22.0
4150	G41500	7750	1482	1586	10	444		11.7	41.8	n.a.	n.a.
4320	G43200	7750	1062	1241	15	360		11.3	n.a.	n.a.	n.a.
4337	G43370	7750	965	1448	14	435		11.3	n.a.	n.a.	n.a.
4340	G43400	7750	475–1379	745–1512	12–22	217–445	16–52	12.3	n.a.	n.a.	n.a.
4615	G46150	7750	517	689	18	n.a.		11.5	n.a.	n.a.	n.a.
4620	G46200	7750	655	896	21	n.a.		12.5	44.1	335	n.a.
4640	G46400	7750	1103	1276	14	390		n.a.	n.a.	n.a.	n.a.
4815	G48150	7750	862	1034	18	325		11.5	n.a.	481	26.0
4817	G48170	7750	n.a.	n.a.	15	355		n.a.	n.a.	n.a.	n.a.
4820	G48200	7750	n.a.	n.a.	13	380		11.3	n.a.	n.a.	n.a.
5120	G51200	7750	786	986	13	302		12.0	n.a.	n.a.	n.a.
5130	G51300	7750	1207	1303	13	380		12.2	48.6	494	21.0
5140	G51400	7750	1172	1310	13	375		12.3	45.8	452	22.8
5150	G51500	7750	1434	1544	10	444		12.8	n.a.	n.a.	n.a.
6120	G61200	7750	648	862	21	n.a.		n.a.	n.a.	n.a.	n.a.
6145	G61450	7750	1165	1213	16	429		n.a.	n.a.	n.a.	n.a.
6150	G61500	7750	1234	1289	13	444		12.2	n.a.	n.a.	n.a.
8617	G86170	7750	676	841	n.a.	n.a.		11.9	45.0	481	30.0
8630	G86300	7750	979	1117	14	325		11.3	39.0	449	n.a.
8640	G86400	7750	1262	1434	13	420		13.0	37.6	460	n.a.
8650	G86500	7750	1338	1475	12	423		11.7	37.6	453	n.a.
8720	G87200	7750	676	841	21	245		14.8	37.6	450	n.a.
8740	G87400	7750	1262	1434	13	420		11.3	37.6	448	n.a.
8750	G87500	7750	1338	1476	12	423		14.8	37.6	448	n.a.
9255	G92550	7750	1482	1600	9	477		14.6	46.8	420	n.a.
9261	G92610	7750	1558	1779	10	514		14.6	46.8	502	n.a.

Other properties common to all carbon- and low-alloy steels types. Young's modulus: 201–209 GPa, Coulomb's or shear modulus: 81–82 GPa, bulk or compression modulus: 160–170 GPa; Poisson ratio: 0.27–0.30.

2.1.11.3 Cast Steels

Cast steels are steels that have been cast into sand molds to form finished or semifinished machine parts or other components. Mostly, the general characteristics of steel castings are very comparable to those of wrought steels. Cast and wrought steels of equivalent composition respond similarly to heat treatment and have fairly similar properties. A major difference is that cast steel has a more isotropic structure. Therefore, properties tend to be more uniform in all directions and do not vary according to the direction of hot or cold working as in many wrought-steel products.

Categories. Cast steels are often divided into the following four categories: cast plain carbon steels, (low-)alloy steel castings, heat-resistant cast steels, and corrosion-resistant cast steels, depending on the alloy content and intended service. Like wrought steels, cast plain carbon steels can be divided into three groups: low-, medium-, and high-carbon steels. However, cast carbon steel is usually specified by mechanical properties (primarily tensile strength) rather than composition. Low-alloy steel castings are considered steels with a total alloy content of less than about 8%. The most common alloying elements are manganese, chromium, nickel, molybdenum, vanadium, and small quantities of titanium or aluminum (grain refinement) and silicon (improved corrosion and high-temperature resistance).

2.1.12 Stainless Steels

2.1.12.1 Description and General Properties

In 1821, the French engineer Pierre Berthier observed that a certain amount of chromium added to iron alloys, in addition to enhancing their stiffness, also improved remarkably their corrosion resistance to acids. Almost a century later, in 1909, Léon Guillet and Albert Portevin in France studied independently the microstructure of Fe-Cr and Fe-Cr-Ni alloys. In 1911, the German metallurgist P. Monnartz, following the pioneering activity of his predecessors, explained the passivation mechanism and determined the lowest percentage of chromium required to impart a rustless ability to steels. The new alloy did not corrode or rust when exposed to weather, and the new iron alloy was then simply referred to as *rostfrei Stahl* in Germany, *rustless or rustproof iron* in Great Britain, and *acier inoxyable* in France. However, in the United States and United Kingdom, it was later denoted by the more modern designation still used today, *stainless steel*. In 1913, the first casting of a stainless steel was performed at Sheffield in the United Kingdom.

Stainless steels are a large family of iron-chromium-based alloys (Fe-Cr) that are essentially low-carbon steels containing a high percentage of chromium, at least above 12 wt.% Cr, to impart the same corrosion resistance conferred by pure chromium in chrome plate. This addition of chromium gives the steel its unique corrosion-resistance properties denoted as stainless or rustproof. The chromium content of the steel allows the formation on the steel surface of a passivating layer of chromium oxide. This protective oxide film is impervious, adherent, transparent, and corrosion resistant in many chemical environments. If damaged mechanically or chemically, this film is self-healing when small traces of oxygen are present in the corrosive medium. It is important to note that in order to be corrosion resistant, the Fe-Cr alloy must contain at least 12 wt.% Cr and that when this percentage is decreased, for instance by precipitation of chromium carbide during heating, the protection is lost and the rusting process occurs. Moreover, the corrosion resistance and other useful properties of stainless steels are largely enhanced by increasing the chromium content usually well above 12 wt.% Cr. Hence the chromium content is usually 15 wt.%, 18 wt.%, 20 wt.%, and even up to 27 wt.% Cr in certain grades. In addition, further alloy additions (e.g., Mo, Ti, S, Cu) can be made to tailor the chemical composition in order to meet the needs of

different corrosion conditions, operating temperature ranges, and strength requirements or to improve weldability, machinability, and work hardening. Generally, the corrosion resistance of stainless steels is, as a rule, improved by increasing the alloy content. The terminology heat resistant and corrosion resistant is highly subjective and somewhat arbitrary. The term heat-resistant alloy commonly refers to oxidation-resistant metals and alloys (see Ni-Cr-Fe alloys in the nickel and nickel alloys section), while corrosion resistant is commonly applied only to metals and alloys that are capable of sustained operation when exposed to attack by corrosive media at service temperatures below 315°C. They are normally Fe-Cr or Fe-Cr-Ni ferrous alloys and can normally be classified as stainless steels. There are roughly more than 60 commercial grades of stainless steel available, and the global annual production was roughly 25 million tonnes in 2004.

2.1.12.2 Classification of Stainless Steels

Following a classification introduced by Zapffe and later modernized to accommodate new grades, stainless steels can be divided into five distinct classes (see Table 2.20). Each class is identified by the alloying elements that affect their microstructure and for which each is named. These classes are as follows:

- (i) austenitic stainless steels;
- (ii) ferritic stainless steels;
- (iii) martensitic stainless steels;
- (iv) duplex or austenoferritic stainless steels; and
- (v) precipitation-hardened (P-H) stainless steels.

In practice, empirical parameters called nickel and chromium equivalents can be utilized to assess the relative stability of austenite and ferrite, respectively. These equivalents are defined as follows:

$$Eq(Ni) = w_{Ni} + 30 \times w_C + 0.5 w_{Mn},$$
$$Eq(Cr) = w_{Cr} + w_{Mo} + 1.5 w_{Si} + 0.5 w_{Nb},$$

where w_i denotes the mass fraction of the chemical element indicated by the subscript. The Ni and Cr equivalents are usually used to assess the phase formation in weldments. Hence modifying the chemistry of the weld metal can ensure a better result by avoiding hot cracking.

Table 2.20. Classification of stainless steels by microstructure		
Type		Typical composition
STAINLESS STEELS	Martensitic stainless steels	12–18 wt.% Cr carbon < 1.2 wt.% C
	Ferritic stainless steels	17–30 wt.% Cr carbon < 0.2 wt.% C
	Austenitic stainless steels	18–25 wt.% Cr 8–20 wt.% Ni
	Duplex stainless steels	18–26 wt.% Cr 4–7 wt.% Ni 2–3 wt.% Mo
	Precipitation-hardening (P-H) stainless steels	12–30 wt.% Cr (Al, Ti, Mo)

after Zapffe, C.-A. (1949) *Stainless Steels*. American Society for Metals (ASM), Materials Park, OH, p. 368.

2.1.12.3 Martensitic Stainless Steels

Martensitic stainless steels (i.e., AISI 400 series) are typically iron-chromium-carbon (Fe-Cr-C) alloys that contain at least 12 and up to 18 wt.% Cr and may have small quantities of additional alloying elements. The carbon content usually ranges between 0.07 and 0.4 wt.% C and in all cases must be lower than 1.2 wt.% C. The high carbon content expands the gamma loop in Fe-Cr phase diagram and hence the crystal structure transforms into austenite upon heating, allowing hardening of the steel by quenching. These steels are called martensitic owing to the distorted body-centered cubic crystal lattice structure in the hardened condition. Martensitic stainless steels exhibit the following common characteristics:

- (i) they have a martensitic crystal structure;
- (ii) they are ferromagnetic;
- (iii) they can be hardened by heat treatment (quenching);
- (iv) they have high strength and moderate toughness in the hardened-and-tempered condition;
- (v) they have poor welding characteristics.

Forming should be done in the annealed condition. Martensitic stainless steels are less resistant to corrosion than the austenitic or ferritic grades. Two types of martensitic steels, AISI 416 and AISI 420F, have been developed specifically for good machinability. Martensitic stainless steels are used where strength and/or hardness are of primary concern and where the environment is not too corrosive. These alloys are typically used for bearings, molds, cutlery, medical instruments, aircraft structural parts, and turbine components. The most commonly used grade is AISI 410; grade AISI 420 is used extensively in cutlery for making knife blades, and grade AISI 440C is used when very high hardness is required. Grade AISI 420 is used increasingly for molds for plastics and for industrial components requiring hardness and corrosion resistance. The physical properties of selected martensitic stainless steels are listed in Table 2.21.

2.1.12.4 Ferritic Stainless Steels

Ferritic stainless steel alloys (i.e., AISI 400 series) exhibit a chromium content ranging from 17 to 30 wt.% Cr but have a lower carbon level, usually less than 0.2 wt.% C, than martensitic stainless steels. Ferritic stainless steels exhibit the following common characteristics:

- (i) they exhibit a body-centered cubic ferrite crystal lattice due to the high chromium content;
- (ii) they are ferromagnetic and retain their basic microstructure up to the melting point if sufficient Cr and Mo are present;
- (iii) they cannot be hardened by heat treatment, and they can be only moderately hardened by cold working; hence they are always used in the annealed condition;
- (iv) in the annealed condition, their strength is ca. 50% higher than that of carbon steels;
- (v) like martensitic steels, they have poor weldability.

Ferritic stainless steels are typically used where moderate corrosion resistance is required and where toughness is not a major need. They are also used where chloride stress-corrosion cracking (SCC) may be a problem because they have high resistance to this type of corrosion failure. In heavy sections, achieving sufficient toughness is difficult with the higher alloyed ferritic grades. Typical applications include automotive trim and exhaust systems and heat-transfer equipment for the chemical and petrochemical industries. The two common grades are grade AISI 409, used for high-temperature applications, and grade AISI 430, the most widely used grade.

Table 2.21. Physical properties of martensitic stainless steels

AISI type	UNS	Average chemical composition (/ wt.%)	Density (ρ /kg.m ⁻³)	Yield strength 0.2% proof (σ_{ys} /MPa)	Ultimate tensile strength (σ_{UTS} /MPa)	Elongation (Z/%)	Rockwell hardness (/HRB)	Coef. lin. thermal exp. (α /10 ⁻⁶ K ⁻¹)	Thermal cond. (k /W.m ⁻¹ .K ⁻¹)	Electrical resist. (ρ /μΩ.cm)
403	S40300	Fe-12.25Cr-1Mn-0.5Si-0.15C-0.6Ni	7800	205–620	485–825	12–20	88	n.a.	n.a.	n.a.
410	S41000	Fe-12.5Cr-1Mn-1Si-0.15C-0.75Ni-0.04P-0.03S	7800	275–620	450–825	12–20	95	9.9	24.9	57
410 Cb	S41040	Fe-11.9Cr-0.24Si-0.19Mn-0.15Nb-0.12C-0.027Mo-0.021P-0.04S	7730	503–1034	655–1248	15–26	HRB 89–HRC32	5.5	24.8	57
410 S	S41008	Fe-12.5Cr-1Mn-1Si-0.6Ni-0.08C	7800	205–240	415–450	22	95	n.a.	n.a.	n.a.
414	S41400	Fe-12.5Cr-1.88Ni-1Mn-1Si-0.15C	7800	620	795–1030	15	n.a.	10.4	24.9	70
416	S41600	Fe-13Cr-1.25Mn-1Si-0.6Mo-0.15C	7800	275	485–1210	20	n.a.	9.9	24.9	57
416 Plus X	S41610	Fe-13Cr-2Mn-1Si-0.6Mo-0.15C	7800	n.a.	585–1210	n.a.	n.a.	n.a.	n.a.	n.a.
416 Se	S41623	Fe-13Cr-1.25Mn-1Si-0.6Mo-0.15C-0.15Se	7800	275	845	20	n.a.	n.a.	n.a.	n.a.
420	S42000	Fe-13Cr-1Mn-1Si-0.15C-0.04P-0.03S	7740	276–1344	483–1586	8–25	HRB 88–HRC 55	10.2	24.9	55
420 FSe	S42023	Fe-13Cr-1Mn-1.25Si-0.15C-0.15Se	7800	1480	1720	8–15	96	n.a.	n.a.	n.a.
422	S42200	Fe-12.5Cr-1Mo-1Mn-1W-0.75Ni-0.75Si-0.22C	7800	585–760	825–965	13–17	n.a.	11.2	23.9	59

Table 2.22. Physical properties of ferritic stainless steels

AISI type	UNS	Average chemical composition (/ wt. %)	Density ($\rho/\text{kg.m}^{-3}$)	Yield strength 0.2% proof (σ_{ys}/MPa)	Ultimate tensile strength (σ_{UTS}/MPa)	Elongation (Z/%)	Rockwell hardness (/HRB)	Coef. linear thermal exp. ($\alpha/10^{-6} \text{ K}^{-1}$)	Thermal cond. ($k/\text{W.m}^{-1}.\text{K}^{-1}$)	Electrical resistivity ($\rho/\mu\Omega.\text{cm}$)
405	S40500	Fe-13Cr-1Mn-1Si-0.2Al-0.6Ni-0.2Al-0.08C-0.04P-0.03S	7800	170–280	415–480	20	88	10.8	27.0	60
409	S40900	Fe-11.125Cr-1Mn-1Si-0.5Ni-0.48Ti-0.08C-0.045P-0.03S	7612	207	380–415	20–25	76	11.7	n.a.	60
429	S42900	Fe-15Cr-1Mn-1Si-0.75Ni-0.12C	7800	205–275	450–480	20–22	88	10.3	25.6	59
430	S43000	Fe-17Cr-1Mn-1Si-0.75Ni-0.12C-0.04P-0.03S	7800	205–275	415–480	30	88	10.4	26.1	60
430F	S43020	Fe-17Cr-1.25Mn-1Si-0.6Mo-0.12C	7800	275	485–860	20	n.a.	10.4	26.1	60
430FSe	S43023	Fe-17Cr-1.25Mn-1Si-0.15Se-0.12C	7800	275	485–860	20	n.a.	10.4	26.1	60
430 Ti	S43036	Fe-18Cr-1Mn-1Si-0.75Ni-0.75Ti-0.1C	7800	310	515	30	n.a.	10.4	26.1	60
434	S43400	Fe-17Cr-1Mn-1Si-1Mo-0.12C	7800	365–315	530–545	23–33	83–90	10.4	26.3	60
436	S43600	Fe-17Cr-1Mn-1Si-1Mo-0.12C-0.7(Ta+Nb)	7800	365	530	23	83	9.3	23.9	60
439	S43900	Fe-18Cr-1.1Ti-1Mn-1Si-0.5Ni-0.15Al-0.07C	7700	205–275	450–485	20–22	88	10.4	24.2	63
442	S44200	Fe-20.5Cr-1Mn-1Si-0.6Ni-0.2C	7800	275–310	515–550	20	90–95	n.a.	n.a.	n.a.
444	S44400	Fe-18.5Cr-1Ni-1Mn-1Si-2Mo-0.025C	7800	275	415	20	95	10.0	26.8	62
446	S44600	Fe-25Cr-1.5Mn-1Si-0.25N-0.2C	7500	275	480–515	16–20	95	10.8	20.9	67
E-Brite 26-1	S44627	Fe-26Cr-1Mo-0.5Ni-0.4Mn-0.4Si-0.2Cu-0.2Nb-0.01C	7800	275	450	16–22	90	n.a.	n.a.	n.a.
Monit 25-4-4	S44635	Fe-25Cr-4Ni-4Mo-1Mn-0.75Si-0.025C	7800	515–550	620–650	20	100	n.a.	n.a.	n.a.
Sea-cure (SC-1)	S44660	Fe-26Cr-2.5Ni-1Mn-1Si-3Mo-0.025C	7800	380–450	550–585	18–20	100	n.a.	n.a.	n.a.
AL 29-4C	S44735	Fe-29Cr-4Mo-1Mn-0.75Si-0.5Ni-0.025C	7800	415	550	20	98	n.a.	n.a.	n.a.
AL 29-4-2	S44800	Fe-29Cr-4Mo-2Ni-0.3Mn-0.2Si-0.15Cu-0.025C	7800	380–415	480–550	15–20	98	n.a.	n.a.	n.a.

Other properties common to all ferritic stainless steel types: Young's modulus: 200–215 GPa; Coulomb's or shear modulus: 80–83 GPa; Poisson ratio: 0.27–0.29; specific heat capacity: ca. 460 J.kg⁻¹.K⁻¹.

2.1.12.5 Austenitic Stainless Steels

Austenitic stainless steels, which exhibit the unique austenite crystal structure even at room temperature, are the largest and most popular family of stainless steels. They were discovered around 1910 when nickel was added to chromium-bearing iron alloys. Actually, austenitic stainless steels are iron-chromium-based alloys containing at least 18 wt.% or more Cr; in addition, they also contain sufficient nickel and/or manganese to stabilize and insure a fully austenitic metallurgical crystal structure at all temperatures ranging from the cryogenic region to the melting point of the alloy. Carbon content is usually less than 0.15 wt.% C. As a general rule, they exhibit the common following characteristics:

- (i) they possess an austenitic crystal lattice structure;
- (ii) by contrast with other classes, they are not ferromagnetic even after severe cold working;
- (iii) they cannot be hardened by heat treatment;
- (iv) they can be hardened by cold working;
- (v) they have better corrosion resistance than other classes;
- (vi) they can be easily welded;
- (vii) they possess an excellent cleanability and allow excellent surface finishing;
- (viii) they exhibit excellent corrosion resistance to several corrosive environments at both room and high temperatures.

However, the austenitic stainless steels have some limitations:

- (i) the maximum service temperature under oxidizing conditions is 450°C; above this temperature heat-resistant steels are required;
- (ii) they are suitable only for low concentrations of reducing acid such HCl; super austenitics are required for higher acid concentration;
- (iii) in service and shielded areas, there might not be enough oxygen to maintain the passive oxide film and crevice corrosion might occur, in which case they must be replaced by super austenitics or duplex and super ferritic steels;
- (iv) very high levels of halide ions, especially the chloride ion, can lead to the breakdown of the passivating film.

It is important to note that upon heating carbon combines with chromium to form chromium carbide. If the chromium content falls below the critical percentage of 10.5 wt.% Cr, the corrosion resistance of the alloy is lost.

Austenitic wrought stainless steels are classified according to the *American Iron & Steel Institute* (AISI) into three groups:

- (i) AISI 200 series, i.e., alloys of iron-chromium-nickel-manganese;
- (ii) AISI 300 series, i.e., alloys of iron-chromium-nickel; and
- (iii) nitrogen-strengthened alloys (with the suffix N added to the AISI grade).

Manganese-bearing austenitic stainless steels originated in the early 1930s when shortages of nickel in Germany made it necessary to quickly find a substitute for austenite stabilizers. German metallurgists found that manganese and nitrogen, though less effective than nickel, performed well. Additional work was also conducted in the United States during the Korean War for the same reason. The lower cost and higher strength of manganese stainless steels compared to the 300 series allowed the commercialization of the 200 series despite higher processing costs due to their higher work-hardening rate. Nitrogen-strengthened austenitic stainless steels are alloys of chromium-manganese-nitrogen; some grades also contain nickel. The yield strengths of these alloys in the annealed condition are typically 50% higher

than those of the non-nitrogen-bearing grades. Like carbon, nitrogen increases the strength of a steel, but unlike carbon, nitrogen does not combine significantly with chromium in a stainless steel. This combination, which forms chromium carbide, reduces the strength and the corrosion resistance of an alloy. Because of their valuable structural and corrosion-resistance properties, this group is the most widely used alloy group in the process industry. Actually, because nickel-bearing austenitic types have the highest general corrosion resistance, they are more corrosion resistant than lower-nickel compositions. Hence, austenitic stainless steels are generally used where corrosion resistance and toughness are primary requirements. Typical applications include shafts, pumps, fasteners, and piping for servicing in seawater and equipment for processing chemicals, food, and dairy products. However, galling and wear are the most common failure modes that require special attention with austenitic stainless steels because these materials serve in many harsh environments. They often operate, for example, at high temperatures, in food-contact applications, and where access is limited. Such restrictions prevent the use of lubricants, leading to metal-to-metal contact, a condition that promotes galling and accelerated wear.

The most widely used grades of austenitic steels are AISI 304 (Fe-18Cr-10Ni), which are the most versatile grade, refractory grade AISI 310 (Fe-25Cr-20Ni) for high-temperature applications, grade AISI 316L (Fe-17Cr-12Ni-2.5Mo) with improved corrosion resistance, and finally AISI 317 (Fe-17Cr-13Ni-3.5Mo) for the best corrosion resistance in chloride-containing media. The largest single alloy in terms of total industrial usage is AISI 304. The effects of some minor alloying elements on the properties of stainless steels are explained schematically in Table 2.23. The major physical properties of austenitic stainless steels are listed in Table 2.24 (see page 104).

Table 2.23. Schematic impact of minor alloying additions on general-purpose stainless steel 300 series			
Property required		Minor element addition	Typical grade
General -purpose stainless steel AISI 304 (Fe-18Cr-8Ni)	Machinability	Sulfur (S) addition	AISI 303
	Weldability	Low-carbon grades	AISI 304L
	Corrosion resistance	Molybdenum (Mo) addition	AISI 316
	Formability	Copper (Cu) addition	AISI 302
after Magee, J. (2002) Development of type 204 Cu stainless steel, a low-cost alternate to type 304. <i>Wire J. Int.</i> , pp. 84–90.			

2.1.12.6 Duplex Stainless Steels

When the chromium content is high (i.e., 18 to 26 wt.% Cr) and the nickel content is low (i.e., 4 to 7 wt.% Ni), the resulting structure is called duplex. In addition, most grades contain 2 to 3 wt.% Mo. This results in a structure that is a combination of both ferritic and austenitic, hence the name duplex. The most common grade is the AISI 2205. They have the following characteristics:

- (i) high resistance to stress-corrosion cracking;
- (ii) increased resistance to chloride ion attack;
- (iii) high weldability;
- (iv) higher tensile and yield strengths than austenitic or ferritic stainless steels.

See Table 2.25, page 106.

2.1.12.7 Precipitation-Hardening Stainless Steels

Precipitation-hardening stainless steels, widely known under the common acronyms PH or P-H, develop very high strength through a low-temperature heat treatment that does not significantly distort precision parts. Compositions of most P-H stainless steels are balanced to produce hardening by an aging treatment that precipitates hard, intermetallic compounds and simultaneously tempers the martensite. The beginning microstructure of P-H alloys is austenite or martensite. The austenitic alloys must be thermally treated to transform austenite into martensite before precipitation hardening can be accomplished. These alloys are used where high strength, moderate corrosion resistance, and good fabricability are required. Typical applications include shafting, high-pressure pumps, aircraft components, high-temper springs, and fasteners.

See Table 2.26, page 107.

2.1.12.8 Cast Heat-Resistant Stainless Steels

Cast stainless steels usually have corresponding wrought grades that have similar compositions and properties. However, there are small but important differences in composition between cast and wrought grades. Stainless steel castings should be specified by the designations established by the Alloy Casting Institute (ACI) and not by the designation of similar wrought alloys. The service temperature provides the basis for a distinction between heat-resistant and corrosion-resistant cast grades. The C series of ACI grades designates the corrosion-resistant steels, while the H series designates the heat-resistant steels, which can be used for structural applications at service temperatures between 650 and 1200°C. The carbon and nickel contents of the H-series alloys are considerably higher than those of the C series. H-series steels are not immune to corrosion, but they corrode slowly, even when exposed to fuel-combustion products or atmospheres prepared for carburizing and nitriding. C-series grades are used in valves, pumps, and fittings. H-series grades are used for furnace parts and turbine components.

2.1.12.9 Processing and Melting Process

The feedstock used in the melting process is essentially made from stainless steel scrap, i.e., scrap arising from sheet-metal fabrication and discarded plant and equipment. This approach enables the economical recycling of valuable alloys by the steel industry. After the chemical identification and analysis of the incoming steel scrap, scrap is sorted by grade, and a charge is prepared adding various alloys of chromium, nickel, and molybdenum depending on the stainless type to produce with an alloy content that is as close as possible to the final grade required for the steel. The scrap charge is then fed into an electric arc furnace, where carbon electrodes are in contact with recycled stainless scrap. Under a high-voltage difference, a current is passed through the electrodes providing sufficient energy to melt the charge. The furnace is connected to a pot lined with refractory ceramic material that resists the high temperatures encountered in the melting process. The molten material from the electric furnace is then transferred into an argon-oxygen decarbonization vessel, where the carbon levels are reduced and the final alloy additions, i.e., nickel, ferrochromium, and ferromolybdenum, are made to achieve the exact desired chemical composition of the final steel. Then the furnace is emptied into a tapping ladle by tilting the furnace forward. The ladle is an open-topped container lined with refractories. The melt is then transferred to a converter, where the steel is refined or purified of impurities of mainly carbon, silicon, and sulfur. This process involves blowing a mixture of oxygen and argon through the melt from the bottom of the converter.

Table 2.24. Physical properties of austenitic stainless steels (annealed)

AISI type	UNS	Average chemical composition (/ wt.%)	Density (ρ /kg.m ⁻³)	Yield strength 0.2% proof (σ_{ys} /MPa)	Ultimate tensile strength (σ_{UTS} /MPa)	Elongation (Z/%)	Rockwell hardness (/HRB)	Coef. linear thermal exp. (α /10 ⁻⁶ K ⁻¹)	Thermal conductivity (k /W.m ⁻¹ .K ⁻¹)	Electrical resistivity (ρ /μΩ.cm)
20Cb-3		Fe-34Ni-20Cr-2.5Mo-2Mn-1Si-0.06C-0.035P-0.035S-1(Nb+Ta)	8080	317-331	627-641	38-45	86-90	14.69	12.2	108.2
201	S20100	Fe-17Cr-4.5Ni-0.25N-6.5Mn-1Si-0.15C	7800	275-965	515-1280	9-40	100	15.7	16.2	69
202	S20200	Fe-18Cr-8.75Mn-5Ni-0.25N-1Si-0.15C	7800	260-515	515-860	12-40	100	17.5	16.2	69
204Cu	S20430	Fe-16.5Cr-7.8Mn-2.5Ni-0.6Si-0.2Mo-0.2Cu-0.2N-0.09C	7800	366	718					
205	S20500	Fe-17.25Cr-1.5Ni-0.35N-14.75Mn-1Si-0.15C	7800	450-475	790-830	40	100	17.9	16.2	69
301	S30100	Fe-17Cr-7Ni-2Mn-1Si-0.15C	8000	205-965	620-1280	9-40	88-95	17.9	16.2	72
302	S30200	Fe-18Cr-9Ni-2Mn-1Si-0.15C	8000	205-965	515-1275	4-40	88-92	17.2	16.2	72
302B	S30215	Fe-18Cr-9Ni-2Mn-2.5Si-0.15C	8000	205-310	515-620	30-40	95	16.2	15.9	72
303	S30300	Fe-18Cr-9Ni-2Mn-1Si-0.6Mo-0.15C	8000	205-240	515-1000	40	n.a.	17.2	16.2	72
303Se	S30323	Fe-18Cr-9Ni-2Mn-1Si-0.15C-0.15Se	8000	205-240	515-1000	40	n.a.	17.2	16.2	72
304	S30400	Fe-19Cr-9.25Ni-2Mn-1Si-0.1N-0.08C-0.045P-0.03S	8000	205-760	515-1035	7-40	92	17.8	16.2	72

Table 2.26. Physical properties of P-H stainless steels

AISI type	UNS	Average chemical composition (/ wt.%)	Density ($\rho/\text{kg.m}^{-3}$)	Young's modulus (E/GPa)	Yield strength 0.2% proof (σ_{ys}/MPa)	Ultimate tensile strength (σ_{UTS}/MPa)	Elongation (Z/%)	Rockwell hardness (/HRC)	Coefficient linear thermal expansion ($a/10^{-6} \text{ K}^{-1}$)	Thermal conductivity ($k/\text{W.m}^{-1}.\text{K}^{-1}$)	Electrical resistivity ($\rho/\mu\Omega.\text{cm}$)
15-5PH	S15500	Fe-14.75Cr-4.5Ni-3.5Cu-1Mn-1Si-0.2Nb-0.07C	7800	196	515–1170	795–1310	10–18	40–48	10.8	17.8	77
17-4PH	S17400	Fe-16.5Cr-4Ni-4Cu-1Mn-1Si-0.2Nb-0.07C	7800	196	515–1170	795–1310	10–18	40–48	10.8	18.3	80
17-7PH	S17700	Fe-17Cr-7.13Ni-1Mn-1Al-1Si-0.09C	7800	204	965–1590	1170–1650	1–7	41–44	11.0	16.4	83
AM350 (Type 633)	S35000	Fe-16.5Cr-4.5Ni-1Mn-2.7Mo-0.5Si-0.07C	7800	n.a.	1000–1030	1140–1380	2–12	36–42	n.a.	n.a.	n.a.
AM355 (Type 634)	S35500	Fe-16.5Cr-4.5Ni-0.75Mn-2.7Mo-0.5Si-0.07C	7800	n.a.	1030–1070	1170–1310	10–12	37	n.a.	n.a.	n.a.
Custom450	S45000	Fe-15Cr-6Ni-1Mn-1Si-0.7Mo-1.5Cu-0.05C	7800	n.a.	515–1100	860–1240	6–18	26–39	n.a.	n.a.	n.a.
Custom455	S45500	Fe-11.75Cr-8.5Ni-0.5Mn-0.5Si-0.7Ti-1.5Cu-0.05C	7800	n.a.	1280–1520	1410–1620	4–10	44–47	n.a.	n.a.	n.a.
P-H 13-8Mo	S13800	Fe-12.75Cr-8Ni-2Mo-1Al-0.2Mn-0.2Si-0.05C	7800	203	585–1410	860–1520	10–16	26–45	10.6	14.0	102

Samples are taken from the melt and analyzed, and the chemical composition of the steel can, if necessary, be modified by the addition of alloying metals in the converter or in the ladle afterwards. Later, the desired molten metal is either cast into ingots or continually cast into a slab or billet form. Then the material is hot-rolled or forged into its final form. Some material receives cold rolling to further reduce the thickness as in sheets or drawn into smaller diameters as in rods and wire. Most stainless steels receive a final annealing and acid pickling in order to remove furnace scale from annealing, and they help to promote the passive surface film that naturally occurs.

2.1.12.10 Simplified Selection of Stainless Steels

Three parameters are important to consider when selecting a particular grade of stainless steel for a given application. These parameters are in order of decreasing importance:

Corrosion resistance. This is the most important property to consider when selecting a stainless steel. Actually, the corrosion resistance is always the primary reason when considering Fe-Cr-Ni alloys. For best results, the maximum allowable corrosion rate, usually 50 $\mu\text{m}/\text{year}$ (2 mils per year), along with an exact knowledge of the corrosive environment, must be known.

Mechanical strength. The mechanical strength is the second most important parameter, especially for designing structural applications.

Fabrication. The capabilities of the stainless steel to be machined, welded, cold worked, and heat treated are, in combination with the two previous parameters, an important parameter to take into account from a technical and a cost-assessment point of view.

Based on an approach developed by the company Carpenter Specialty Alloys⁸, it is possible to summarize the selection process graphically (Figure 2.3), plotting the grade of the stainless steel as a function of both corrosion resistance and mechanical strength.

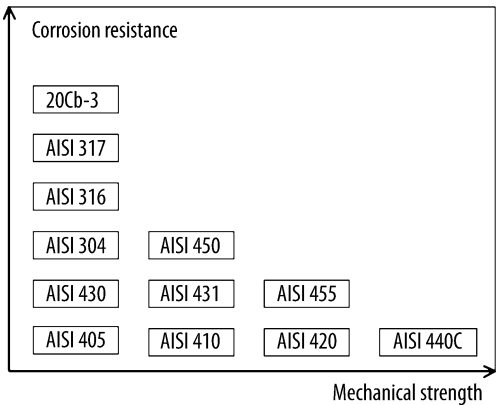


Figure 2.3. Stainless steel selection chart

⁸ Collective (1969) *Simplifying stainless steel selection with Carpenter's Selectally® method*. Carpenter Technology, Reading, PA.

2.1.12.11 Stainless Steel Application Guidelines

Table 2.27. Guide for selected stainless steels (corrosion, oxidation, fabrication, application)

Grade	Corrosion
201	High work-hardening rate; low-nickel equivalent of type 301. Flatware, automobile wheel covers, trim.
202	General-purpose low-nickel equivalent of type 302. Kitchen equipment, hub caps, milk handling.
205	Lower work-hardening rate than type 202; used for spinning and special drawing operations. Nonmagnetic and cryogenic parts.
301	High work-hardening rate; used for structural applications where high strength plus high ductility are required. Railroad cars, trailer bodies, aircraft structurals, fasteners, automobile wheel covers and trim, pole line hardware.
302	General-purpose austenitic stainless steel. Trim, food-handling equipment, aircraft cowlings, antennas, springs, cookware, building exteriors, tanks, hospital and household appliances, jewelry, oil-refining equipment, signs.
302B	More resistant to scale than type 302. Furnace parts, still liners, heating elements, annealing covers, burner sections.
303	Free-machining modification of type 302, for heavier cuts. Screw machine products, shafts, valves, bolts, bushings, nuts.
303Se	Free-machining modification of type 302, for lighter cuts; used where hot working or cold heading may be involved. Aircraft fittings, bolts, nuts, rivets, screws, studs.
304	Low-carbon modification of type 302 for restriction of carbide precipitation during welding. Chemical and food processing equipment, brewing equipment, cryogenic vessels, gutters, downspouts, flashings.
304Cu	Lower work-hardening rate than type 304. Severe cold-heading applications.
304L	Extra-low-carbon modification of type 304 for further restriction of carbide precipitation during welding. Coal hopper linings, tanks for liquid fertilizer and tomato paste.
304N	Higher nitrogen than type 304 to increase strength with minimum effect on ductility and corrosion resistance, more resistant to increased magnetic permeability. Type 304 applications requiring higher strength.
305	Low work-hardening rate; used for spin forming, severe drawing, cold heading, and forming. Coffee urn tops, mixing bowls, reflectors.
308	Higher-alloy steel having high corrosion and heat resistance. Welding filler metals to compensate for alloy loss in welding, industrial furnaces.
309	High-temperature strength and scale resistance. Aircraft heaters, heattreating equipment, annealing covers, furnace parts, heat exchangers, heat-treating trays, oven linings, pump parts.
309S	Low-carbon modification of type 309. Welded constructions, assemblies subject to moist corrosion conditions.
310	Type 310 provides excellent corrosion resistance and heat resistance plus good strength at room and elevated temperatures. It is essentially nonmagnetic as annealed and becomes slightly magnetic when cold worked. It has a high corrosion resistance to sulfite liquors and is useful for handling nitric acid, nitric-sulfuric acid mixtures, and acetic, citric, and lactic acids. Oxidation resistance is good up to the scaling temperature of 1093°C, and below that temperature it can be used in both continuous and intermittent service. Typical uses include furnace parts, heating elements, aircraft and jet-engine parts, heat exchangers, carburizing-annealing boxes, sulfite liquor-handling equipment, kiln liners, boiler baffles, refinery and chemical-processing equipment, auto-exhaust parts.
314	More resistant to scale than type 310. Severe cold-heading or cold-forming applications. Annealing and carburizing boxes, heat-treating fixtures, radiant tubes.

Table 2.27. (continued)

Grade	Corrosion
316	Higher corrosion resistance than types 302 and 304; high creep strength. Chemical and pulp handling equipment, photographic equipment, brandy vats, fertilizer parts, ketchup cooking kettles, yeast tubs.
316L	Extra-low-carbon modification of type 316. Type 316L is a molybdenum-containing austenitic stainless steel intended to provide improved corrosion resistance relative to type 304L in moderately corrosive process environments, particularly those containing chlorides or other halides. Welded construction where intergranular carbide precipitation must be avoided. Type 316 applications require extensive welding. Type 316L has been used in handling many chemicals used by the process industries, including pulp and paper, textile, food, pharmaceutical, medical, and other chemical-processing equipment.
316F	Higher phosphorus and sulfur than type 316 to improve machining and nonseizing characteristics. Automatic screw machine parts.
316N	Higher nitrogen than type 316 to increase strength with minimum effect on ductility and corrosion resistance. Type 316 applications require extra strength.
317L	Extra-low-carbon modification of type 317 for restriction of carbide precipitation during welding with improved corrosion and creep resistance in strongly corrosive process environments, particularly those containing chlorides or other halides such as those encountered in pulp and paper mills. The low carbon permits 317L to be welded without sensitization to intergranular corrosion resulting from chromium carbide precipitation in the grain boundaries. Type 317L is nonmagnetic in the annealed condition but may become slightly magnetic as a result of welding. Dyeing and ink manufacturing equipment.
321	Type 321 is similar to 304 but with titanium addition five times the carbon content that reduces carbide precipitation during welding and in 425–815°C service. It has excellent corrosion resistance toward most chemicals and oxidation resistance up to 815°C. Aircraft exhaust manifolds, boiler shells, process equipment, expansion joints, cabin heaters, fire walls, flexible couplings, pressure vessels.
329	Austenitic-ferritic type with general corrosion resistance similar to type 316 but with better resistance to stress-corrosion cracking; capable of age hardening. Valves, valve fittings, piping, pump parts.
330	Good resistance to carburization and oxidation and to thermal shock. Heat-treating fixtures.
347	Similar to type 321 with higher creep strength. Airplane exhaust stacks, welded tank cars for chemicals, jet-engine parts.
348	Similar to type 321; low retentivity. Tubes and pipes for radioactive systems, nuclear-energy uses.
384	Suitable for severe cold heading or cold forming; lower cold-work-hardening rate than type 305. Bolts, rivets, screws, instrument parts.
403	Turbine-quality grade. Steam turbine blading and other highly stressed parts including jet-engine rings.
405	Nonhardenable grade for assemblies where air-hardening types such as 410 or 403 are objectionable. Annealing boxes, quenching racks, oxidation-resistant partitions.
409	General-purpose construction stainless. Greater protection than carbon steels and coated steels but lower than 304. Rusting occurs at inclusion sites resulting from titanium stabilization leading to problems of cosmetic appearance only. Corrosion resistance of HAZ is comparable to that of the base metal and is superior to 410. The destructive scaling in air starts at 789°C, this is the general maximum service temperature for continuous exposure in air. Good fabricating characteristics. Can be cut, blanked, and formed without difficulty. Automotive and truck exhaust systems, tubular manifolds, transformer and capacitor cases, agricultural spreaders, gas turbine exhaust silencers, heat exchangers.

Table 2.27. (continued)

Grade	Corrosion
410	General-purpose heat-treatable type. Machine parts, pump shafts, bolts, bushings, coal chutes, cutlery, hardware, jet engine parts, mining machinery, rifle barrels, screws, valves.
410 Cb	The corrosion resistance of type 410 Cb stainless steel is the same as type 410 as demonstrated in laboratory tests and actual service. The tempering characteristics of 410 Cb offer an advantage over type 410 in resistance to stress corrosion cracking. To develop similar tensile strengths, a higher tempering temperature is used with 410 Cb. The higher temperature results in more effective relief of residual internal stresses that, in some environments, promote stress-corrosion cracking.
414	High-hardenability steel. Springs, tempered rules, machine parts, bolts, mining machinery, scissors, ships' bells, spindles, valve seats.
416	Free-machining modification of type 410, for heavier cuts. Aircraft fittings, bolts, nuts, fire extinguisher inserts, rivets, screws.
416Se	Free-machining modification of type 410, for lighter cuts. Machined parts require hot working or cold heading.
420	Type 420 provides corrosion resistance similar to 410 plus increased strength and hardness. It is magnetic in both the annealed and hardened conditions. Provides full corrosion resistance only in the hardened or hardened and stress-relieved conditions. In these conditions, its corrosion resistance is similar to that of 410. The alloy is not normally used at temperatures exceeding 427°C due to rapid softening and loss of corrosion resistance. It resists corrosion by the atmosphere, fresh water, mine water, steam, carbonic acid, crude oil, gasoline, perspiration, alcohol, ammonia, mercury, sterilizing solutions, soaps, and other similar corrosive media. Heat treatments. Annealing: for maximum softness, heat uniformly to 816–899°C and cool slowly. Process annealing: heat to 732–788°C, air cool. Hardening: preheat, then heat to 982–1066°C, soak at temperature, and air cool or quench in warm oil. Stress relieving: heat at 149–427°C for 1 to 3 h, cool in air or quench in oil or water. Typical uses include cutlery, surgical and dental instruments, scissors, tapes, and straight edges.
420F	Free-machining modification of type 420. Applications similar to those for type 420 requiring better machinability.
422	High strength and toughness at service temperatures up to 1200°F. Steam turbine blades, fasteners.
429	Improved weldability as compared to type 430. Nitric acid and nitrogen-fixation equipment.
430	General-purpose nonhardenable chromium type. Has excellent corrosion resistance, including high resistance to nitric acid as well as to sulfur gases and many organic and food acids. This alloy does not provide the resistance to pitting by dilute reducing acids that is provided by the chromium-nickel stainless steels. Heat and oxidation resistance with a maximum scaling temperature of 815°C. Decorative trim, nitric acid tanks, annealing baskets, combustion chambers, dishwashers, heaters, mufflers, range hoods, recuperators, restaurant equipment.
430F	Free-machining modification of type 430, for heavier cuts. Screw machine parts.
430FSe	Free-machining modification of type 430, for lighter cuts. Machined parts requiring light cold heading or forming.
431	Special-purpose hardenable steel used where particularly high mechanical properties are required. Aircraft fittings, beater bars, paper machinery, bolts.
434	Modification of type 430 designed to resist atmospheric corrosion in the presence of winter road conditioning and dust-laying compounds. Automotive trim and fasteners.
436	Similar to types 430 and 434. Used where low “roping” or “ridging” required. General corrosion and heat-resistant applications such as automobile trim.

Table 2.27. (continued)

Grade	Corrosion
440A	Hardenable to higher hardness than type 420 with good corrosion resistance. Cutlery, bearings, surgical tools.
440B	Cutlery grade. Cutlery, valve parts, instrument bearings.
440C	Yields highest hardnesses of hardenable stainless steels. Balls, bearings, races, nozzles, balls and seats for oil-well pumps, valve parts.
442	High-chromium steel, principally for parts that must resist high service temperatures without scaling. Furnace parts, nozzles, combustion chambers.
446	High resistance to corrosion and scaling at high temperatures, especially for intermittent service; often used in sulfur-bearing atmosphere. Annealing boxes, combustion chambers, glass molds, heaters, pyrometer tubes, recuperators, stirring rods, valves.
501	Heat resistance; good mechanical properties at moderately elevated temperatures. Heat exchangers, petroleum-refining equipment.
502	More ductility and less strength than type 501. Heat exchangers, petroleum-refining equipment, gaskets.
SAF 2205	SAF 2205 with equal amounts of ferrite and austenite is a duplex stainless steel that exhibits a high strength, low thermal expansion, and higher thermal conductivity than austenitic steels. SAF 2205 has a high resistance to stress corrosion cracking, corrosion fatigue, and erosion. The addition of nitrogen provides a further increase in pitting and crevice corrosion resistance. SAF 2205 offers very good resistance even in acids that have a fairly high halide content. It has good weldability and can be welded using most of the welding techniques for stainless steels. Heat exchangers, tubes and pipes for production and handling of gas and oil, in desalination plants. Pressure vessels, pipes, tanks and heat exchangers for processing and transport of various chemicals or handling solutions containing chlorides.
SAF 2304	SAF 2304 has a high strength, high resistance to stress corrosion cracking, a low thermal expansion, and a high thermal conductivity. The high chromium content provides good and uniform corrosion resistance, even to pitting and crevice corrosion. In very strongly oxidizing acids such as nitric acid, SAF 2304 is often more resistant than molybdenum-alloyed steels. Additional properties are a good weldability and workability and a high impact strength. Hot-water tanks, water heaters, cargo containers, fire and blast walls on offshore platforms, heat-exchanger tubing, hydraulic piping, digesters, evaporators.
SAF 2507	SAF 2507 is a ferritic-austenitic stainless steel combining the most desirable properties of both ferritic and austenitic steels. The high chromium and molybdenum contents provides very high resistance to pitting, crevice, and uniform corrosion. The duplex microstructure results in good resistance to stress corrosion cracking. The mechanical strength is also very high. SAF 2507 can be used in dilute hydrochloric acid. Pitting is normally not a problem in the area below the boundary line, but crevices should be avoided.

2.1.13 High-Strength Low-Alloy Steels (HSLA)

High-strength low-alloy steels, usually denoted by the common acronym HSLA, represent a specific group of steels in which enhanced mechanical properties and, sometimes, resistance to atmospheric corrosion are obtained by the addition of moderate amounts of one or more alloying elements other than carbon. They were developed primarily for the automotive industry to replace low-carbon steels in order to improve the strength-to-weight ratio and meet the need for higher-strength construction-grade materials, particularly in the as-rolled condition. Different types are available, some of which are carbon-manganese steels, and others contain further alloy additions governed by special requirements for weldability,

formability, toughness, strength, and cost. In practice, HSLA steels are especially characterized by their mechanical properties, obtained in the as-rolled condition, and must exhibit a minimum yield strength of 275 MPa or higher. Such high strength is usually attained through the addition of small amounts of alloying elements, and hence several of these steels exhibit enhanced atmospheric corrosion resistance. Typically, HSLA steels are low-carbon steels containing up to 1.5 wt.% Mn, strengthened by small additions of columbium, copper, vanadium, or titanium and sometimes by special rolling and cooling techniques. Improved-formability HSLA steels contain additions such as zirconium, calcium, or rare-earth elements for sulfide-inclusion shape control. While additions of elements such as copper, silicon, nickel, chromium, and phosphorus improve atmospheric corrosion resistance, they also increase their cost. They are not intended for quenching and tempering. For certain applications, however, they are sometimes annealed, normalized, or stress relieved with some influence on mechanical properties. In addition, most HSLA alloys exhibit directionally sensitive properties. For instance, formability and impact strength vary significantly for some grades depending on whether the material is tested longitudinally or transversely to the rolled direction. Where these steels are used for fabrication by welding, care must be exercised in the selection of grade and in the details of the welding process. Certain grades may be welded without preheat or postheat. Forming, drilling, sawing, and other machining operations on

Table 2.28. Description of selected grades of HSLA steels

HSLA grade	Description
Grade 942X	A niobium- or vanadium-treated carbon-manganese high-strength steel similar to 945X and 945C except for somewhat improved welding and forming properties.
Grade 945A	An HSLA steel with excellent welding characteristics, both arc and resistance, and the best formability, weldability, and low-temperature notch toughness of the high-strength steels. It is generally used in sheets, strip, and light plate thicknesses.
Grade 945C	A carbon-manganese high-strength steel with satisfactory arc welding properties if adequate precautions are observed. It is similar to grade 950C, except that lower carbon and manganese improve arc welding characteristics, formability, and low-temperature notch toughness at some sacrifice in strength.
Grade 945X	A niobium- or vanadium-treated carbon-manganese high-strength steel similar to 945C, except for somewhat improved welding and forming properties.
Grade 950A	An HSLA steel with good weldability, both arc and resistance, with good low-temperature notch toughness, and good formability. It is generally used in sheet, strip, and light plate thicknesses.
Grade 950B	An HSLA steel with satisfactory arc welding properties and fairly good low-temperature notch toughness and formability.
Grade 950C	A carbon-manganese high-strength steel that can be arc-welded with special precautions, but is unsuitable for resistance welding. The formability and toughness are fair.
Grade 950D	An HSLA steel with good weldability, both arc and resistance, and fairly good formability. Where low-temperature properties are important, the effect of phosphorus in conjunction with other elements present should be considered.
Grade 950X	A niobium- or vanadium-treated carbon-manganese high-strength steel similar to 950C, except for somewhat improved welding and forming properties.
Grades 955X, 960X, 965X, 970X, 980X	These are steels similar to 945X and 950X with higher strength obtained by increased amounts of strengthening elements, such as carbon or manganese, or by the addition of nitrogen up to about 0.015%. This increased strength entails reduced formability and usually decreased weldability. Toughness will vary considerably with composition and mill practice.

HSLA steels usually require 25 to 30% more energy than do structural carbon steels. Commercially HSLA steels are available in all standard wrought forms (i.e., sheet, strip, plate, structural shapes, bar-size shapes, and special shapes).

HSLA alloys can be grouped into four classes:

- (i) as-rolled carbon-manganese steels;
- (ii) high-strength low-alloy steels;
- (iii) heat-treated carbon steels;
- (iv) heat-treated low-alloy steels.

Over 20 types of these commercial high-strength alloy steels are produced. Some have been developed to combine improved welding characteristics along with high strength. Most have good impact properties in addition to high strength. An example of the high-yield-strength grades are HY-80 and HY-100, which is used for naval vessels. This material combines high strength and toughness with weldability.

HSLA alloys are particularly attractive for transportation-equipment components where weight reduction is important. Because of their high strength-to-weight ratio, abrasion resistance, and, for certain compositions, improved atmospheric corrosion resistance, these steels are adapted particularly for use in mobile equipment and other structures where substantial weight savings are generally desirable. Common applications are, for instance, in a typical

Table 2.29. Mechanical properties of high-strength low-alloy (HSLA) steels

Usual and trade name	Density ($\rho/\text{kg.m}^{-3}$)	Min. Yield strength 0.2% proof (σ_{ys}/MPa)	Min. ultimate tensile strength (σ_{UTS}/MPa)	Elongation (Z/%)
ASTM A242	7750	290–345	435–480	18
ASTM A517	7750	620–690	760–895	18
ASTM A572	7750	290–450	415–550	15–20
ASTM A588	7750	290–345	435–485	18
ASTM A606	7750	310–345	450–480	21–22
ASTM A607	7750	310–485	410–590	14–22
ASTM A618	7750	290–380	430–655	18–23
ASTM A633	7750	290–415	430–690	18–23
ASTM A656	7750	345–550	415–620	12–20
ASTM A715	7750	345–550	415–620	16–24
ASTM A808	7750	290–345	415–450	18–22
ASTM A871	7750	415–450	520–550	15–18
SAE 942X	7750	290	415	20
SAE 945C	7750	275–310	415–450	18–19
SAE 950 A	7750	290–345	430–483	18
SAE 955 X	7750	380	483	17
SAE 960 X	7750	415	520	16
SAE 970 X	7750	485	590	15
SAE 980 X	7750	550	655	10
HY-80	7750	550–690	n.a.	17–20
HY-130	7750	895–1030	n.a.	14–15

passenger car such as door-intrusion beams, chassis members, reinforcing and mounting brackets, steering and suspension parts, bumpers, and wheelstruck bodies, while other applications include frames, structural members, scrapers, truck wheels, cranes, shovels, booms, chutes, conveyors, trucks, construction equipment, and off-road vehicles. Mining equipment and other heavy-duty vehicles use HSLA sheets or plates for chassis components, buckets, grader blades, and structural members outside the body. Structural forms are specified in applications such as offshore oil and gas rigs, single-pole power-transmission towers, railroad cars, and ship construction.

2.1.14 Ultrahigh-Strength Steels

Ultrahigh-strength structural steels must exhibit a minimum yield strength above 1380 MPa. Ultrahigh-strength steels start with grade 4340, and the other grades are modifications of this alloy. When these steels are used for aerospace components, they are usually produced by the vacuum-arc-remelt (VAR) process. They are classified into several broad categories based on chemical composition or metallurgical-hardening mechanisms. Medium-carbon alloy steels are generally modifications of grade 4330 or 4340, usually with increased molybdenum, silicon, and/or vanadium. These grades provide excellent hardenability in thick sections. Type H13, which includes modified tool steels of the H11 hot-work tool-steel varieties, provides the next step in increased hardenability and greater strength. Most steels in this group are air hardened in moderate to large sections and therefore are not likely to distort or quench crack. Structural uses of these steels are not as widespread as they once were, mainly because of the development of other steels costing about the same but offering greater fracture toughness.

2.1.15 Tool and Machining Steels

Tool steels, owing to their relatively high hardness, were developed in certain carbon-, medium-, and low-alloy steels through compositional adjustments or quenching and tempering at relatively low temperatures. These steels are used for applications that require:

- (i) resistance to wear/abrasion;
- (ii) thermal shock resistance;
- (iii) stability during heat treatment;
- (iv) strength at high temperatures; and
- (v) toughness.

Tool steels are increasingly being used for machining tools and dies. Tool steels are melted in relatively small batches in electric furnaces and produced with careful attention to homogeneity. They can be further refined by techniques such as argon/oxygen decarburization (AOD), vacuum arc melting (VAM), or electroslag refining (ESR). Because of the high alloy content of certain groups, tool steels must be rolled or forged with care to produce satisfactory bar products. To develop their best properties, tool steels are always heat treated. Because the parts may distort during heat treatment, precision parts should be semifinished, heat treated, then finished. Severe distortion is most likely to occur during liquid quenching, so an alloy should be selected that provides the needed mechanical properties with the least severe quench. Tool steels are classified according to the American Institute of Steel and Iron (AISI) designation into several broad groups, some of which are further divided into subgroups according to alloy composition, hardenability, or mechanical similarities.

Table 2.30. AISI designation of tool steels

Class	AISI type	Description
Air-hardening medium-alloy tool steels (cold worked)	A	Air-hardening medium-alloy tool steels are best suited for applications such as machine ways, brick mold liners, and fuel-injector nozzles. The air-hardening types are specified for thin parts or parts with severe changes in cross section, i.e., parts that are prone to crack or distort during hardening. Hardened parts from these steels have a high surface hardness; however, these steels should not be specified for service at elevated temperatures.
Air-hardening high carbon and chromium (cold worked)	D	Air-hardening high-chromium and carbon tool steels possess high wear resistance and high hardenability and exhibit little distortion. They are best suited for applications such as machine ways, brick mold liners, and fuel-injector nozzles. The air-hardening types are specified for thin parts or parts with severe changes in cross section, i.e., parts that are prone to crack or distort during hardening. Hardened parts from these steels have a high surface hardness; however, these steels should not be specified for service at elevated temperatures.
Hot-work steels	H	Hot-work tool steels, due to the addition of tungsten and molybdenum, exhibit good heat and abrasion resistance from 315 to 540°C. Hence, they serve well at elevated temperatures. However, although these alloys do not soften at these high temperatures, they should be preheated before and cooled slowly after service to avoid cracking. Note the chromium-containing grades are less expensive than the tungsten and molybdenum grades. For instance, the chromium grades H11 and H13 are used extensively for aircraft parts such as primary airframe structures, cargo support lugs, catapult hooks, and elevator hinges. Subgroups are divided according to H10 to H19: chromium grades, H21 to H26: tungsten grades, H41 to H43: molybdenum grades.
Low-alloy tool steels	L	Low-alloy tool steels are often specified for machine parts when wear resistance combined with toughness is required.
High-speed-tool steels (molybdenum alloy)	M	Molybdenum alloy high-speed-tool steels are the best known tool steels because they exhibit both abrasion and heat resistance, though not toughness. Hence they make good cutting tools because they resist softening and maintain a sharp cutting edge due to high hardness until high service temperatures. This characteristic is sometimes called “red heat hardness.” These deep-hardening alloys, in which cobalt additions improve cutting, are used for steady, high-load conditions rather than shock loads. Note that tempering at about 595°C increases toughness. Typical applications are pump vanes and parts for heavy-duty strapping machinery.
Oil-hardening cold-work tool steels	O	Oil-hardening cold-work tool steels are expensive but can be quenched less drastically than water-hardening types.
Mold tool steels	P	These are special-purpose tool steels containing chromium and nickel as major alloying elements. They exhibit low hardness and low resistance to work hardening when annealed.
Shock-resisting tool steels	S	Shock-resistant tool steels, with Cr-W, Si-Mo, and Si-Mn as major alloys, are strong and tough, but they are not as wear resistant as many other tool steels. These steels resist sudden and repeated loadings. Applications include pneumatic tooling parts, chisels, punches, shear blades, bolts, and springs subjected to moderate heat in service.

Table 2.30. (continued)

Class	AISI type	Description
High-speed-tool steels (tungsten alloys)	T	Tungsten-alloy high-speed-tool steels are the best known tool steels because they exhibit both abrasion and heat resistance, though not toughness. Hence they make good cutting tools because they resist softening and maintain a sharp cutting edge due to high hardness until high service temperatures. This characteristic is sometimes called “red heat hardness.” These deep-hardening alloys, in which cobalt additions improve cutting, are used for steady, high-load conditions rather than shock loads. Note that tempering at about 595°C increases toughness. Typical applications are pump vanes and parts for heavy-duty strapping machinery.
Water-hardening, or carbon, tool steels	W	Water-hardening tool steels containing 0.6 wt.% to 1.4 wt.% C are widely used because they combine low cost, a good toughness, and excellent machinability. They are available as shallow, medium, or deep hardening, so the specific alloy selected depends on part cross section and required surface and core hardnesses. Common applications include drills, shear knives, chisels, hammers, and forging dies.

The effects of the most common alloying elements on the properties of tool steel are briefly summarized below.

Carbon (C). For unalloyed tool steels, the concentration of carbon is usually above 0.60 wt.% C. Carbon is an essential and ubiquitous alloying element that imparts hardenability of steels. Raising the carbon content up to 1.3 wt.% C also increases the wear resistance considerably, although to the detriment of fracture toughness.

Manganese (Mn). Small additions of manganese up to 0.60 wt.% Mn are added to reduce brittleness and to improve forgeability of steels. Larger amounts of manganese improve hardenability, allowing oil quenching for unalloyed carbon steels, thereby reducing deformation.

Silicon (Si). Because silicon comes from ferrosilicon used in the deoxidizing treatment of steels, silicon is not considered an alloying element of tool steels. However, silicon improves its hot-forming properties. In combination with other alloying elements, the silicon content is sometimes raised up to 2 wt.% Si to increase the strength and fracture toughness of steels that must withstand heavy shock loads.

Tungsten (W). Tungsten is one of the most important alloying elements of tool steels, particularly because it imparts a “hot hardness,” that is, the resistance of the steel to the softening effect of elevated temperature, and it forms hard and abrasion-resistant tungsten carbides (e.g., WC and W_2C), thus improving the wear properties of tool steels.

Vanadium (V). Vanadium contributes to the refinement of the carbide structure and thus improves the forgeability of tool steels. Moreover, vanadium exhibits a strong tendency to form hard carbides (e.g., VC and V_2C), which improves both the hardness and the wear properties of tool steels. However, an excessive amount of vanadium carbides makes the grinding of the tool steel extremely difficult, imparting a low grindability.

Molybdenum (Mo). A minute amount of molybdenum improves certain metallurgical properties of alloy steels such as deep hardening and fracture toughness. Molybdenum is used often in larger amounts in certain high-speed-tool steels to replace tungsten, primarily for economic reasons, often with nearly equivalent results.

Cobalt (Co). Cobalt increases the hot hardness of tool steels. Substantial addition of cobalt, however, raises the critical quenching temperature of the steel with a tendency to increase the decarburization of the surface and reduces toughness.

Table 2.31. Physical properties of tool steels

AISI type	UNS	Average chemical composition (/ wt.%)	Density (ρ /kg.m ⁻³)	Yield strength 0.2% proof (σ_{ys} /MPa)	Ultimate tensile strength (σ_{UTS} /MPa)	Elongation (Z/%)	Rockwell hardness scale C (/HRC)	Coefficient of linear thermal expansion (α /10 ⁻⁶ K ⁻¹)	Thermal conductivity (k /W.m ⁻¹ .K ⁻¹)	Quench medium	Annealing (/°C)	Hardening (/°C)	Tempering (/°C)
Air-hardening tool steels													
A2	T30102	Fe-5Cr-1C-1Mn-1Mo-0.35V-0.5Si	7860	n.a.	n.a.	n.a.	57-62	10.7	n.a.	A	845-870	925-980	175-540
A6	T30106	Fe-2.2Mn-1.2Mo-1Cr-0.7C-0.5Si	7840	n.a.	n.a.	n.a.	54-60	11.5	n.a.	A	730-745	830-870	150-425
A7	T30107	Fe-5.4Cr-4.5V-2.4C-0.8Mn-1.1Mo-0.5Si-1W	7660	n.a.	n.a.	n.a.	58-66	12.0	n.a.	A	870-900	955-980	150-540
A8	T30108	Fe-5.1Cr-1.4Mo-1.25W-1Si-0.55C-0.5Mn	7870	n.a.	n.a.	n.a.	48-57	n.a.	n.a.	A	845-870	980-1010	175-595
A9	T30109	Fe-1.25Cr-0.5Mn-1.8Ni-1.5Mo-1Si	7780	n.a.	n.a.	n.a.	40-56	12.0	n.a.	A	845-870	980-1025	510-620
A10	T30110	Fe-1.25C-1.35Mn-1.8Ni-1.5Mo-1.25Si	7680	n.a.	n.a.	n.a.	52-62	12.8	n.a.	A	765-795	790-815	175-425
Air-hardening cold-work steels													
D2	T30402	Fe-12Cr-1.5C-1.1V-0.6Mn	7700	n.a.	n.a.	n.a.	58-64	10.4	n.a.	A	870-900	980-1025	205-540
D3	T30403	Fe-12Cr-1.5C-1.1V-0.6Mn	7700	n.a.	n.a.	n.a.	58-64	12.0	n.a.	O	870-900	925-980	205-540
D5	T30405	Fe-12Cr-1.5C-1.1V-0.6Mn-0.9Mo-0.6Si	7700	n.a.	n.a.	n.a.	58-64	11.0	n.a.	A	870-900	970-1010	205-540
D7	T30407	Fe-12Cr-1.5C-4.1V-0.6Mn	7700	n.a.	n.a.	n.a.	58-64	12.2	n.a.	A	870-900	1010-1065	150-540
Hot-work tool steels													
H11	T20811	Fe-5.1Cr-1Si-1.4Mo-0.45V	7750	n.a.	n.a.	n.a.	38-55	11.9	42	A	845-900	995-1025	540-650
H13	T20813	Fe-5.1Cr-1V-1.4Mo-0.3C	7760	1290-1570	1495-1960	13-15	40-53	10.4	29	A	845-900	995-1040	540-650
H21	T20821	Fe-9.25W-0.3Mn-3.4Cr-0.45V	8280	n.a.	n.a.	n.a.	40-55	12.4	27	A, O	870-900	1095-1205	595-675
H42	T20842	Fe-6.13W-4Cr-5Mo-2V-0.6C	8150	n.a.	n.a.	n.a.	50-60	11.0	n.a.	O, A, S	845-900	1120-1220	565-650
Low-alloy tool steels													
L2	T61202	Fe-1Cr-0.5Si-0.73C-0.5Mn-0.25Mo	7860	510-1790	710-2000	5-25	30-54	11.3	n.a.	O, W	760-790	845-925	175-315
L6	T6106	Fe-1.6Ni-0.9Cr-0.5Si-0.7C-0.5Mn-0.5Mo	7860	380-1790	655-2000	4-25	32-54	11.3	n.a.	O	760-790	790-845	175-540

Chromium (Cr). Chromium is added from a few percent to high-alloy tool steels and up to 12 wt.% Cr to types in which chromium is the major alloying element. Chromium improves hardenability and, together with high carbon content, provides both wear resistance and fracture toughness. However, high chromium content raises the hardening temperature of the tool steel and thus can make it prone to hardening deformations. A high percentage of chromium also affects the grindability of tool steels.

Nickel (Ni). Nickel is usually used in combination with other alloying elements, such as chromium, to improve the fracture toughness and, to some extent, the wear resistance of tool steels.

2.1.16 Maraging Steels

Maraging steels are a particular class of extra-low-carbon (i.e., < 0.03 wt.% C) and nickel-rich (i.e., 18 wt.% < Ni < 22 wt.%) iron alloys having an ultrahigh strength. Nickel is the major alloying element followed by cobalt, which is added up to 12 wt.% to accelerate precipitation reactions, molybdenum, and, to a lesser extent, titanium, aluminum, and copper. A typical example of a maraging steel is an iron alloy with the following composition: 17 to 19 wt.% Ni, 7 to 9 wt.% Co, 4.5 to 5.0 wt.% Mo, and 0.6 to 0.9 wt.% Ti. Alloys of this type are

Table 2.32. Composition and selected physical properties of maraging steels (ASTM A538)

Maraging steel grade	Chemical composition (wt.%)	Density (ρ /kg.m ⁻³)	Melting range (°C)	Young's elastic modulus (E/GPa)	Yield strength 0.2% proof (σ_{ys} /MPa)	Ultimate tensile strength (σ_{UTS} /MPa)	Elongation (Z/%)	Fracture toughness (K_{IC} /MPa.m ^{-1/2})	Vickers hardness (HV)	Coefficient linear thermal expansion (α /10 ⁻⁶ K ⁻¹)	Thermal conductivity (k /W.m ⁻¹ .K ⁻¹)	Specific heat capacity (c_p /J.kg ⁻¹ .K ⁻¹) (50-100°C)	Electrical resistivity (ρ /μΩ.cm)
Grade 200	Fe-18Ni-8Co-3.2Mo-0.2Ti-0.1Al-0.03C	8000			1340	1390	11		450				
Grade 250 ⁹	Fe-18Ni-8Co-5Mo-0.4Ti-0.1Al-0.03C	8000	1430-1450	186	1620	1700	8-9		520	10.1	19.7		65
Grade 300	Fe-18Ni-12Co-5Mo-0.6Ti-0.1Al-0.03C	8000			1810	1930	7		570				
Grade 350	Fe-18.8Ni-10.8Co-4.22Mo-1Ti	8000			2318	2339	8.0	76.6					
Grade 1800	Fe-18.5Ni-3Mo-1.26Ti	8000			1647	1696	13.1	46.2					
Grade 2000	Fe-18.9-4.1Mo-1.93Ti	8000			1957	2017	8.0	74.0					
Grade 2800	Fe-17.9Ni-14.8Co-6.69Mo-1.1Ti	8000			2617	2693	6.0	31.6					

⁹ G = 71 GPa, ν = 0.30, melting range: 1430-1450°C

hardened to martensite and then tempered at 480 to 500°C. The tempering results in strong precipitation hardening owing to the precipitation of intermetallics from the martensite, which is supersaturated with the alloying elements. By analogy with the precipitation hardening in aluminum, copper, and other nonferrous alloys, this process has been termed aging, and since the initial structure is martensite, the steels have been called maraging. Because of the negligible carbon content, the peculiar strengthening behavior of these steels does not rely at all on the usual precipitation of iron carbide common to all carbon steels. Indeed, the strength relies only on the precipitation of the metastable nickel-rich intermetallic phases: Ni_3Mo and Ni_3Ti . Moreover, the high dispersion of these precipitates ensures a superior strength without loss of malleability. Major suitable characteristics of maraging steels are listed below:

- (i) ultrahigh strength at room temperature;
- (ii) simple heat treatment with minimum shrinkage;
- (iii) superior fracture toughness compared to quenched and tempered steels;
- (iv) low carbon content, which precludes decarburization issues;
- (v) ease of machining, high surface finish, and good weldability;
- (vi) good corrosion resistance and crack propagation.

Therefore, maraging steels are required in applications requiring ultrahigh strength along with a good dimensional stability during heat treatment. Typical applications are gears, fasteners, rocket and missile cases, aircraft parts, plastic mold dies or shafts, as a substitute for long, thin, carburized, or nitrided parts, and for components subject to impact fatigue, such as print hammers or clutches. Compositions and selected properties of three common grades of maraging steels are listed in Table 2.32.

2.1.17 Iron-Based Superalloys

Iron-, nickel-, and cobalt-based alloys used primarily for high-temperature applications are known as superalloys. The iron-based grades, which are less expensive than cobalt- or nickel-based grades, are of three types:

- (i) alloys that can be strengthened by a martensitic type of transformation;
- (ii) alloys that are austenitic and are strengthened by a sequence of hot and cold working, usually forging at 1100 to 1150°C followed by finishing at 650 to 880°C;
- (iii) austenitic alloys strengthened by precipitation hardening.

Some metallurgists consider only the last group to be superalloys, the others being categorized as high-temperature, high-strength alloys. In general, the martensitic types are used at temperatures below 540°C, while the austenitic types are used above 540°C. The American Institute of Steel and Iron (AISI) designation defined the AISI 600 series and divided superalloys into six subclasses of iron-based alloys:

- (i) AISI 601 to 604: martensitic low-alloy steels;
- (ii) AISI 610 to 613: martensitic secondary hardening steels;
- (iii) AISI 614 to 619: martensitic chromium steels;
- (iv) AISI 630 to 635: semiaustenitic and martensitic P-H stainless steels;
- (v) AISI 650 to 653: austenitic steels strengthened by hot/cold work;
- (vi) AISI 660 to 665: austenitic superalloys; all grades except alloy 661 are strengthened by second-phase precipitation.

Iron-based superalloys are characterized by both high-temperature and room-temperature strength and resistance to creep, oxidation, corrosion, and wear. Wear resistance increases with carbon content. Maximum wear resistance is obtained in alloys 611, 612, and 613, which are used in high-temperature aircraft bearings and machinery parts subjected to sliding contact. Oxidation resistance increases with chromium content. The martensitic chromium steels, particularly alloy 616, are used for steam-turbine blades. The superalloys are available in all conventional mill forms (i.e., billet, bar, sheet, and forgings), and special shapes are available for most alloys. In general, austenitic alloys are more difficult to machine than martensitic types, which machine best in the annealed condition. Crack sensitivity makes most of the martensitic steels difficult to weld by conventional methods. These alloys should be annealed or tempered prior to welding; even then, preheating and postheating are recommended. Welding drastically lowers the mechanical properties of alloys that depend on hot/cold work for strength. All of the martensitic low-alloy steels machine satisfactorily and are readily fabricated by hot working and cold working. The martensitic secondary-hardening and chromium alloys are all hot worked by preheating and hot forging. Austenitic alloys are more difficult to forge than the martensitic grades.

2.1.18 Iron Powders

Powder metallurgy (P/M) parts are made to net shape by compacting iron metal powders in special dies and sintering them to achieve the final properties desired. These properties depend on the alloy, the shape of the powder particles, the compressive strength, and the sintering temperature. Three basic steps are usually encountered in a P/M process:

- (i) filling the loose powder into a die;
- (ii) compaction under pressure and ejection of the green compressed part;
- (iii) sintering of the workpiece in a furnace under reducing atmosphere.

Three major quantities are used in P/M: the **bulk density** of the loose iron powder (e.g., 3000 kg.m⁻³ for water-atomized powder) which is lower than the **apparent density** due to air space. After compression, the compressed density doubles to about 6000 kg.m⁻³. Finally, after sintering, the fusion that occurs between particles increases the steel's density to a density approaching the **theoretical density** or **pore-free density**. Three types of iron powders are available commercially.

2.1.18.1 Water-Atomized Iron Powders

Water-atomized iron powder was first introduced industrially in the 1960s by the A.O. Smith Company in the USA. Iron metal or iron alloy is first melted between 1100°C and 1650°C, depending on the carbon content, and then poured into a ceramic vessel with a small plugged hole in the bottom. When the ceramic plug is removed, the molten metal falls, forming a narrow stream about 1 in. (2.54 cm) in diameter. Jets of high-pressure water (14 MPa) strike the liquid metal stream at an angle and disintegrate it into fine droplets. Due to the high specific heat capacity of water, the iron droplets freeze into intricate shapes well before surface tension has time to minimize their surfaces into little spheres, as in gas atomization, while their core is dense. Hence the iron particles become highly irregular in shape. As a result, when these powders are compressed under 414 MPa, parts have only 12 vol.% porosity. Moreover, water-atomized iron powders are very pure, which means they are ductile and do not exhibit a foraminous structure like sponge iron. Their coarse pores are easier to collapse, and thus water-atomized powders are easier to compress and are known for their good flow rates into dies and their ability to pack well.

2.1.18.2 Gas-Atomized Iron Powders

Gas-atomized iron powders are produced by melting iron metal between 1100°C and 1540°C, depending on the carbon content, and then pouring it into a tundish with a small plugged hole in the bottom. When the ceramic plug is removed, the molten metal falls, forming a narrow stream about 2 cm in diameter. Jets of high-pressure inert gas such as argon or nitrogen strike the liquid metal stream at a given angle and disintegrate it into fine droplets. Surface tension causes the liquid droplets to adopt a spherical form. The chamber surrounding the stream is large enough that the metal droplets solidify before reaching the wall of the chamber. Spherical powders have their uses, due to their virtually perfect spherical shape, and gas-atomized powders pour well into dies, but the compaction is straightforward. Actually, even high compressive strength in the range 275 to 690 MPa are not enough to cause them to stick together. They pack so uniformly that in most cases they make a face-centered cubic dense arrangement of balls, even if the high pressures causes the particle to form a weak metallic bond. When the pressure is released, the green form remains too fragile.

2.1.18.3 Sponge-Reduced Iron

Sponge iron powder is obtained by the reduction of mill scale coming from the scale as a by-product from steel mills processing large steel billets. Actually, during heating and working of the hot mill products, the air oxidation of steel produces a poorly adherent black scale of magnetite (Fe_3O_4) called mill scale. The scale thickens and eventually flakes off to land on the floor. The mill scale flakes are then collected and sent to companies specializing in the conversion of mill scale into sponge iron powder. The reduction process consists in putting a layer of mill scale 10 to 15 cm thick onto a belt conveyor made of stainless steel sheet that passes through a reduction furnace at about 930°C. Hydrogen gas is used as reducing atmosphere. Usually hydrogen is produced by steam reforming, water electrolysis, or the cracking of ammonia depending on the facility's proximity to an inexpensive source of hydrogen. The hydrogen gas reduces the magnetite of the mill scale into metallic iron and water vapor. After a few hours the reduction process is complete. Because oxygen is removed from the solid, the final reduced metal exhibits tiny vacancies or pores, giving it a typical porous structure, and for that reason it was called sponge iron. This characteristic of sponge iron ensures an excellent green strength of the pressed material between 276 and 690 MPa. However, today the use of sponge iron powder is declining. Actually, because sponge iron powder particles exhibit a highly angular shape, on pouring it into a die, the particles rub their rough surfaces against each other and flow more slowly. Once they settle in the die, protuberances keep them from packing very closely. To make a part of a given weight, the die has to be much deeper to hold enough powder. Moreover, during pressing, even at a compressive strength of 415 MPa, the final green material has about 19% porosity in the sponge irons, but parts still have high green strength.

2.1.19 Further Reading

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2.2 Nickel and Nickel Alloys

2.2.1 Description and General Properties

Nickel [7440-02-0], chemical symbol Ni, atomic number 28, and relative atomic mass 58.6934(2), is the third element of the upper transition metals of group VIIIB (10) of Mendeleev's periodic chart. It was named after the English Old Nick. Pure nickel is a dense (8902 kg.m^{-3}), tough, silvery-white lustrous metal that exhibits both a high electrical ($6.9 \mu\Omega.\text{cm}$) and thermal conductivity ($90.7 \text{ W.m}^{-1}.\text{K}^{-1}$) and has a high melting point (1455°C). The face-centred cubic (fcc) crystal structure imparts to the metal a good ductility, and nickel can be fabricated readily by the use of standard hot and cold working methods. Like iron and cobalt, pure nickel is a soft ferromagnetic material but with a lower saturation magnetization M_s of $0.480 \times 10^6 \text{ A.m}^{-1}$. However, like iron and cobalt, nickel loses its ferromagnetism above its Curie temperature of 627 K and becomes paramagnetic. From a chemical point of view, pure nickel is corrosion resistant to attack by moist air or water at room temperature and highly resistant to concentrated alkaline solutions or molten alkalis (e.g., NaOH, KOH). However, nickel dissolves in diluted mineral acids such as hydrochloric acid (HCl) and readily in nitric acid (HNO_3). The major reactions of nickel metal with most common acids are summarized in Table 2.33.

Nickel metal reacts only slowly with fluorine gas due to the self-formation of a thin protective passivating layer of nickel fluoride (NiF_2). Therefore nickel and cupronickel alloys such as Monel®400 and K-500 are used extensively for handling fluorine gas, anhydrous hydrogen fluoride, and hydrofluoric acid. Nickel is extensively used in coinage but is more important either as pure metal or in the form of alloys for its many domestic and industrial applications.

Prices (2006). Pure nickel (99.99 wt.% Ni) is priced 18 US\$/kg (8.16 US\$/lb).

2.2.2 History

Nickel was used industrially as an alloying metal almost 2000 years before it was isolated and recognized as a new element. As early as 200 B.C., the Chinese made substantial amounts of a white alloy from zinc and a copper-nickel ore found in Yunnan province. The alloy, known as *pai-t'ung*, was exported to the Middle East and even to Europe. Later, miners in Saxony (Germany) encountered what appeared to be a copper ore but found that processing it yielded only a useless slaglike material. Earlier, an ore of this same type was called *Kupfernickel* because the miners considered it bewitched and ascribed this to the devil, Old Nick, and his mischievous gnomes because, though it resembled copper ore, it yielded

Table 2.33. Reactions of nickel metal with acids

Acid	Soln.	Chemical reaction scheme	Notes
Hydrochloric acid (HCl)	All	$\text{Ni}^0 + 2\text{HCl} \longrightarrow \text{Ni}^{2+} + 2\text{Cl}^- + \text{H}_2(\text{g})$	Dissolves slowly
Sulfuric acid (H_2SO_4)	Dil.	$\text{Ni}^0 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Ni}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	Dissolves slowly
Nitric acid (HNO_3)	Dil.	$3\text{Ni}^0 + 8\text{HNO}_3 \longrightarrow 3\text{Ni}^{2+} + 6\text{NO}_3^- + 2\text{NO}(\text{g}) + 4\text{H}_2\text{O}$	Dissolves readily
	Conc.	No reaction	Does not dissolve due to passivation

a brittle, unfamiliar metal. It was from niccolite, studied by the Swedish chemist and mineralogist Baron Axel Fredrik Cronstedt, that nickel was first isolated and recognized as a new element in 1751. In 1776 it was established that *pai-t'ung*, now called nickel-silver, was composed of copper, nickel, and zinc. Demand for nickel-silver was stimulated in England in about 1844 by the development of silver electroplating, for which it was found to be the most desirable base. The use of pure nickel as a corrosion-resistant electroplated coating developed a little later. Small amounts of nickel were produced in Germany in the mid-19th century. More substantial amounts came from Norway, and a little from a mine at Gap, Pennsylvania in the USA. In 1863, a new large nickel-bearing laterite ore deposit was discovered in New Caledonia. The first production began at the Société Le Nickel in 1877, and it dominated the market until the development in 1885 of the huge copper-nickel orebody of the Copper Cliff in Sudbury, Ontario (Canada). After 1905 the Canadian deposit became the world's largest source of nickel in the 20th century, until the discovery in the late 1970s of the Norilsk complex in the Soviet Union.

2.2.3 Natural Occurrence, Minerals and Ores

Nickel, with a relative abundance in the Earth's crust of 70 mg/kg, is twice as abundant as copper, and the Earth's inner core is supposedly made of a Ni-Fe alloy (see Section 13.2). Nickel never occurs free in nature but only as an alloy with iron in certain meteorites. However, due to its chalcophile geochemical character, like copper, most nickel occurs primarily as minerals in combination with arsenic, antimony, and sulfur. Nickel is mined from two types of ore deposits: primary nickel-bearing sulfide orebodies and secondary nickel-bearing laterite deposits.

- (i) **Primary nickel-bearing sulfide orebodies.** This type of deposit originates from intrusive or volcanic magmatic activity. As a general rule, in sulfidic ores, the nickel content ranges between 0.4 and 2.0 wt.% Ni and the nickel occurs mainly as *pentlandite* $[(\text{Ni},\text{Fe})_9\text{S}_8, \text{cubic}]$ and, to a lesser extent, in nickeloan *pyrrhotite* $[(\text{Fe},\text{Ni})\text{S}_{1-x}, \text{hexagonal}]$, which represent the major nickel lost during the smelting process. In addition to pentlandite and pyrrhotite, nickel also occurs in amounts of less significance in less common sulfides and sulfosalts such as *millerite* $[\text{NiS}, \text{hexagonal}]$, *niccolite* $[\text{NiAs}, \text{hexagonal}]$, *rammelsbergite* $[\text{NiAs}_2, \text{orthorhombic}]$, *gersdorffite* $[\text{NiAsS}, \text{cubic}]$, and *ullmanite* $[\text{NiSbS}, \text{cubic}]$. Traces of nickel are also found in *chalcopyrite* $[\text{CuFeS}_2, \text{tetragonal}]$ and *cubanite* $[\text{CuFe}_2\text{S}_3, \text{orthorhombic}]$. It is important to note that in sulfidic ores, traces of precious metals (e.g., Au, Ag) and of the six platinum group metals (i.e., Ru, Rh, Pd, Os, Ir, and Pt), along with Co, Se, and Te, are always present, and they represent important commercial byproducts. Sulfidic ores are relatively easy to concentrate, and the major orebodies of economic importance are extensively found in Canada (Sudbury), Africa, and Russia (Norilsk). The operating costs for extracting nickel from sulfidic ores are higher than for laterites due to underground mining, but recoverable byproducts ensure the economic feasibility of such deposits.
- (ii) **Secondary nickel-bearing laterite deposits.** Laterites are residual sedimentary rocks such as bauxite resulting from the *in situ* weathering of ultramafic igneous rocks (e.g., peridotite such as dunite). This near-surface alteration, common in tropical climates, exerts an intense leaching action of the host rock, and the soluble nickel cations percolate down and may reach a concentration sufficiently high to make mining economically worthwhile. Owing to this method of formation, nickel-bearing laterite deposits are found near the surface as a soft, frequently claylike material, with nickel concentrated in strata as a result of weathering. The principal nickel-bearing mineral is nickeloan *limonite* $[(\text{Fe},\text{Ni})\text{O}(\text{OH}) \cdot n\text{H}_2\text{O}, \text{orthorhombic}]$ and also a phyllosilicate called

garnierite (formerly *noumeite*) $[(\text{Ni,Mg})_6\text{Si}_4\text{O}_{10}(\text{OH})_8]$, amorphous]. The two major laterite deposits of economic importance are found in New Caledonia and Cuba, while smaller deposits occur in Australia, Indonesia, the Philippines, the Dominican Republic, Colombia, and Brazil. Nickel-bearing laterite deposits account for the major part of nickel reserves but only half of world production.

Other sources of nickel, especially in deep-ocean polymetallic nodules (see Manganese) lying on the Pacific Ocean floor, will probably have an important economic role in the future. As a general rule, to be mineable, a nickel ore deposit must be able to produce annually at least 40,000 tonnes of nickel, that is, 800,000 tonnes for a period of 20 years. Annual world nickel production is 925,000 tonnes (2003), of which 70% is consumed for stainless steels. The world's largest nickel-producing countries are Russia, Canada, New Caledonia, and Australia. In 2005, the major nickel projects were the laterite deposit of Goro (New Caledonia, France) and the sulfide ore deposit of Voisey's Bay (Newfoundland, Canada).

Table 2.34. Annual production capacity of major nickel producers

Company	Annual production (tonnes)
Inco CVRD	220,900
Xstrata (formerly Falconbridge)	113,852
BHP Billiton Ltd.	133,800
Norilsk Nickel	250,000
Sherritt Gordon Mines Ltd.	15,939

2.2.4 Processing and Industrial Preparation

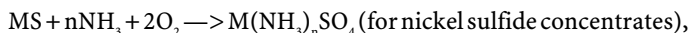
The metallurgy of nickel depends on the type of ore processed, and both pyrometallurgical (smelting) and hydrometallurgical processes are used alone or in combination. As a general rule, the sulfide ore is transformed into nickel(III) sulfide, Ni_2S_3 , which is roasted in air to give nickel(II) oxide, NiO , while the laterite ore is fired to give off nickel oxide. In both processes, the metal is won by carbothermic reduction of the oxide. Some high-purity nickel is made by refining.

Nickel from sulfide ores. Sulfidic nickel-bearing ore deposits are usually mined by underground techniques in a manner similar to that of copper ores. Sulfide ores are crushed and ground in order to liberate nickel-bearing minerals from the inert gangue materials. Afterward, the raw ore is concentrated selectively by common beneficiation processes (e.g., both froth flotation and magnetic separation). After separation from gangue minerals, the ore concentrate contains between 6 and 12 wt.% Ni. For high-copper-containing ores the concentrate is then subjected to a second selective flotation process that produces a low-nickel copper concentrate and a nickel-rich concentrate, each processed in a separate smelting process. Nickel concentrates may be leached either with sulfuric acid or ammonia, or they may be dried, roasted to reduce sulfur and impurities, and smelted in bath processes using electric arc furnaces, as is done with copper. Nickel requires higher smelting temperatures of 1350°C in order to produce an artificial nickel-iron sulfide known as *nickel matte*, which contains 25 to 50 wt.% Ni. The nickel matte can be processed either hydrometallurgically or pyrometallurgically. When processed hydrometallurgically, the matte is cast into anode slabs, and pure nickel cathodes are obtained by electrowinning, or the nickel matte is leached by hydrochloric acid to yield a nickel chloride solution from which the nickel can

be recovered by electrowinning. When processed pyrometallurgically, the iron in the matte is converted in a rotating converter into iron oxide, which combines with a silica to form the slag. The slag is removed, leaving a matte of 70 to 75 wt.% Ni. The conversion of nickel sulfide directly into metal is achieved at a high temperature above 1600°C. The matte is then roasted in air to give the nickel oxide. The nickel metal is obtained by carbothermal reduction of the nickel oxide with coal in an electric arc furnace (EAF) operating between 1360°C and 1610°C.

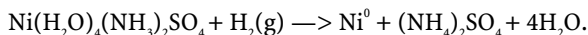
Nickel from lateritic ores. Laterites are usually mined in earth-moving operations, with large shovels, draglines, or front-end loaders extracting the nickel-rich strata and discarding large boulders and waste material. Recovery of nickel from laterite ores is an energy-intensive process requiring high energy input. The ore is then reduced in an electric arc furnace to yield a ferronickel alloy. In addition, laterites are difficult to concentrate by common ore beneficiation processes, and hence a large amount of ore must be smelted to win the metal. Because these ores contain large amounts of water (i.e., 35 to 40 wt.% H₂O), the major operation consists in drying in rotary-kiln furnaces, giving the nickel oxide.

Sheritt ammonia pressure leaching. This hydrometallurgical process was first implemented in 1954 by Sheritt Gordon Mines in Fort Saskatchewan, Alberta, Canada. In this process, the finely ground nickel sulfide concentrates obtained after flotation or the metal matte are reacted at 80 to 95°C in a high-pressure autoclave under 850 kPa with an oxygenated ammonia or ammonia-ammonium sulfate liquor. Ammonia dissolves nickel and, to a lesser extent, cobalt, zinc, and copper by forming soluble ammonia complex cations as follows:



with $M = Ni, Co, Zn, Cu$ and $n = 2-6$.

After removing iron as iron hydroxide and precipitating copper as copper sulfide, nickel is recovered from the leach liquor by reduction with pure hydrogen at 200°C under a high pressure of 3 MPa:



The remaining liquor contains all the cobalt that is recovered by precipitating it as cobalt sulfide with hydrogen sulfide. Finally, the remaining spent solution consists of ammonium sulfate, which is sold as fertilizer.

Refining. The two common refining processes are electrolytic refining and the carbonyl process. Electrowinning uses a sulfate or chloride electrolyte and is performed in electrolyzers with two compartments separated by a diaphragm to prevent the passage of impurities from anode to cathode. During electrolysis, the impure nickel anode(+) is dissolved and nickel electrodeposits onto pure nickel cathodes, while more noble metals (e.g., Au, Ag, and PGMs) are recovered in slurries at the bottom of the reactor and soluble metals (e.g., Fe, Cu) remain in the electrolyte. In the carbonyl refining process, carbon monoxide is passed through the matte, yielding nickel and iron carbonyls [i.e., Ni(CO)₄ and Fe(CO)₅]. After separation, nickel carbonyl is decomposed onto pure nickel pellets to produce nickel shot.

2.2.5 Nickel Alloys

Nickel and the nickel alloys constitute a family of alloys with increasing importance in many industrial applications because they exhibit both a good corrosion resistance in a wide variety of corrosive environments and an excellent heat resistance from low to elevated temperatures. Some types have an almost unsurpassed corrosion resistance in certain media, but

nickel alloys are usually more expensive than, for example, iron-based or copper-based alloys or than plastic construction materials. Nickel alloys are alloys in which nickel is present in greater proportion than any other alloying element. Actually, nickel content throughout the alloy families ranges from 32.5 to 99.5 wt.% Ni. The most important alloying elements are Fe, Cr, Cu, and Mo, and a variety of alloy classes are commercially available. Two groups of nickel-alloy classes can be distinguished: alloys that depend primarily on the inherent corrosion characteristics of nickel itself and alloys that greatly depend on chromium as the passivating alloying element such as for stainless steels. Common nickel-alloy families include commercially pure nickel, binary systems (e.g., Ni-Cu, Ni-Si, and Ni-Mo), ternary systems (e.g., Ni-Cr-Fe, and Ni-Cr-Mo), more complex systems (e.g., Ni-Cr-Fe-Mo-Cu), and superalloys, and they are usually grouped into the following classes:

- (i) commercially pure and high-nickel alloys;
- (ii) nickel-molybdenum alloys;
- (iii) nickel-copper alloys;
- (iv) nickel-chromium alloys;
- (v) nickel-chromium-iron alloys;
- (vi) nickel-chromium-molybdenum alloys;
- (vii) nickel-chromium-iron-molybdenum-copper alloys;
- (viii) nickel superalloys.

Structural applications that require specific corrosion resistance or elevated temperature strength receive the necessary properties from nickel and its alloys. Some nickel alloys are among the toughest structural materials known. Compared to steel, other nickel alloys exhibit both an ultrahigh tensile strength, a high proportional limit, and high Young's moduli. At cryogenic temperatures, nickel alloys are strong and ductile. Several nickel-based superalloys are specified for high-strength applications at temperatures up to 1090°C. High-carbon nickel-based casting alloys are commonly used at moderate stresses above 1200°C. Commercial nickel and nickel alloys are available in a wide range of wrought and cast grades; however, considerably fewer casting grades are available. Wrought alloys tend to be better known by tradenames such as Monel, Hastelloy, Inconel, Incoloy. The casting alloys contain additional elements, such as silicon and manganese, to improve castability and pressure tightness.

See Tables 2.35 and 2.36, pages 129–131.

2.2.6 Nickel Alloys and Superalloys

Nickel-based alloys, which form the bulk of alloys produced, are basically nickel-chrome alloys with a face-centered cubic solid-solution matrix containing carbides and the coherent intermetallic precipitate $\gamma\text{-Ni}_3(\text{Al,Ti})$. This latter precipitate provides most of the alloy strengthening and results in useful operating temperatures up to 90% of the start of melting. Further additions of aluminum, titanium, niobium, and tantalum are made to combine with nickel in the γ' phase, and additions of molybdenum, tungsten, and chromium strengthen the solid solution matrix.

See Table 2.37, pages 132–138.

Table 2.35. Description of main nickel-alloy classes

Nickel alloys class	Description
Commercially pure nickels and extra-high-nickel alloys	Major wrought alloys in this group are commercially pure nickel 200 and 201 grades. The cast grade is recommended for use at temperatures above 315°C owing to its lower carbon content, which prevents graphitization and attendant ductility loss. These two grades are particularly suitable when corrosion resistance to caustic alkaline hydroxides (i.e., NaOH, KOH), high-temperature halogens and hydrogen halides (e.g., HF), and molten fluorides in nonoxidizing conditions are required. These alloys are particularly well suited for food-contact applications. Duranickel® 301, a precipitation-hardened nickel alloy, has excellent spring properties up to 315°C, and corrosion resistance is similar to that of commercially pure wrought nickel. Commercially pure nickel has good electrical, magnetic, and magnetostriuctive properties.
Cupronickels (Ni-Cu)	In this category the most common cupronickel alloys are the Monel®400 and Monel®K-500. The Ni-Cu alloys differ from nickel 200 and 201 because their strength and hardness can be increased by age hardening. Ni-Cu alloys exhibit higher corrosion resistance than commercially pure nickel, especially to sulfuric and hydrofluoric acids, and chloride brines. Handling of waters, including seawater and brackish water, is the major application of these two alloys in the CPI (e.g., desalination plants). In addition, Monel®400 and K-500 are immune to chloride-ion stress-corrosion cracking, which is often considered in their selection.
Ni-Mo	The Ni-Mo binary type, Hastelloy®B-2, offers superior resistance to hydrochloric acid, aluminum-chloride catalysts, and other strongly reducing chemicals. It also has excellent high-temperature strength in inert atmospheres and in a vacuum. The Ni-Mo alloys are commonly used for handling hydrochloric acid in all concentrations at temperatures up to the boiling point. These alloys are produced commercially under the tradenames Hastelloy®B and Chlorimet 2.
Ni-Cr-Fe	Ni-Cr-Fe alloys are known commercially under the common tradenames Haynes®214 and 556, Inconel®600, and Incoloy®800. Haynes®214 has excellent resistance to oxidation up to 1200°C and resists carburizing and chlorine-contaminated atmospheres. Haynes®556 combines effective resistance to sulfidizing, carburizing, and chlorine-bearing environments with good oxidation resistance, fabricability, and high-temperature strength. Inconel®600 exhibits good resistance to both oxidizing and reducing environments. Incoloy®800 has good resistance to oxidation and carburization at elevated temperatures, resists sulfur attack, internal oxidation, scaling, and corrosion in many harsh atmospheres and is suited for severely corrosive conditions at elevated temperatures.
Ni-Cr-Mo	Ni-Cr-Mo are commercially known under the common tradenames Hastelloy®C-276 and C-22 and Inconel® 625. Hastelloy®C-22 has better overall corrosion resistance and versatility than any other Ni-Cr-Mo alloy. In addition, it exhibits outstanding resistance to pitting, crevice corrosion, and stress-corrosion cracking. Hastelloy®C-276 has excellent corrosion resistance to strong oxidizing and reducing corrosives, acids, and chlorine-contaminated hydrocarbons. It is also one of the few materials with titanium that withstands the corrosive effects of wet chlorine gas, hypochlorite, and chlorine dioxide. Present applications include the pulp and paper industry, various pickling acid processes, and production of pesticides and various agrichemicals.

Table 2.35. (continued)

Nickel alloys class	Description
Ni-Cr-Fe-Mo-Cu	Ni-Cr-Fe-Mo-Cu alloys are known commercially under the tradenames Hastelloy®G-30 and H, Haynes®230, Inconel® 617, 625, and 718, and Incoloy®825. Haynes®230 has excellent high-temperature strength and heat and oxidation resistance, making it suitable for various applications in the aerospace, airframe, nuclear, and chemical-process industries. Hastelloy®G-30 has many advantages over other metallic and nonmetallic materials in handling phosphoric acid, sulfuric acid, and oxidizing acid mixtures. Hastelloy®H exhibits a localized corrosion resistance equivalent or better to Inconel®625. In addition, it has good resistance to hot acids and excellent resistance to stress-corrosion cracking. It is often used in flue gas desulfurization equipment. Inconel® 617 resists cyclic oxidation at 1100°C and has good stress-rupture properties above 990°C. Inconel®625 has high strength and toughness from cryogenic temperatures up to 1100°C, good oxidation resistance, exceptional fatigue strength, and good resistance to many corrosives. It is extensively used in furnace mufflers, electronic parts, chemical- and food-processing equipment, and heat-treating equipment. Inconel®718 has excellent strength from -250 to 700°C. The alloy is age hardenable, can be welded in the fully aged condition, and has excellent oxidation resistance up to 1800°C. Incoloy®825 resists pitting and intergranular corrosion, reducing acids, and oxidizing chemicals. Applications include pickling-tank thermowell and bayonet heater, spent-nuclear-fuel-element recovery and radioactive-waste handling, chemical-tank trailers, evaporators, sour-well tubing, hydrofluoric acid production, and pollution-control equipment.
Nickel -based superalloys	Nickel-based superalloys can be classified in three groups. (i) First are those strengthened by intermetallic compound precipitation in a face-centered cubic matrix. These alloys are well known under the common tradenames Astroloy, Udimet®700, and Rene®95. (ii) Another type of nickel-based superalloy is represented by Hastelloy®X. This alloy is essentially solid-solution strengthened. (iii) A third class consists of oxide-dispersion-strengthened (ODS) alloys such as MA-754, which is strengthened by dispersions of yttria coupled with gamma prime precipitation (e.g., MA-6000). Nickel-based superalloys are used in cast and wrought forms, although special processing (e.g., powder metallurgy, isothermal forging) often is used to produce wrought versions of the more highly alloyed compositions such as Udimet®700 or Astroloy®.

Table 2.36. Physical properties of commercially pure and high nickel alloys (annealed)

Usual and trade name	UNS	Average chemical composition (/ wt.%)	Density (ρ /kg.m ⁻³)	Yield strength 0.2% proof (σ_{ys} /MPa)	Ultimate tensile strength (σ_{UTS} /MPa)	Elongation (Z/%)	Brinell hardness (/HB)	Coeff. linear thermal expansion ($a/10^{-6}$ K ⁻¹)	Thermal conductivity ($k/W.m^{-1}.K^{-1}$)	Specific heat capacity ($c_p/J.kg^{-1}.K^{-1}$)	Electrical resistivity ($\rho/\mu\Omega.cm$)
Nickel 200	N02200	99.5	8890	148	462	47	109	13.3	74.9	456	9.5
Nickel 201	N02201	99.6	8890	103	403	50	129	13.1	79.3	456	8.5
Nickel 205	N02205	99.6	8890	90	345	45	80	13.3	75.0	456	9.5
Nickel 211	N02211	93.7Ni-4.75Mn	8890	240	530	40	n.a.	13.3	44.7	532	16.9
Nickel 233	N02233	99.00	8890	150	400	40	100	13.3	n.a.	n.a.	n.a.
Nickel 270	N02270	99.95	8890	60–110	310–345	50	85	13.3	86	460	7.5
Nickel 290	N02290	99.95	8890	n.a.	n.a.	n.a.	n.a.	13.3	n.a.	n.a.	n.a.

Table 2.37. Selected physical properties of nickel-based alloys and superalloys (annealed)

Common and trade name	UNS	Average chemical composition (/ wt.%)	Class	Density (ρ /kg.m ⁻³)	Melting point or range (°C)	Young's modulus (E/GPa)	Yield strength 0.2% proof (σ_{ys} /MPa)	Ultimate tensile strength (σ_{UTS} /MPa)	Elongation (Z/%)	Brinell hardness (/HB)	Coef. linear thermal exp. (α /10 ⁻⁶ K ⁻¹)	Thermal conductivity (k/W.m ⁻¹ .K ⁻¹)	Specific heat capacity (cP/J.kg ⁻¹ .K ⁻¹)	Electrical resistivity (ρ /μΩ.cm)
Alloy 31	N08031	32Fe-31Ni-27Cr-6.5Mo	Fe-Ni-Cr alloys											
Alloy 904L	N08904	25Ni-21Cr-4.5Mo-2Mn-1Si	Fe-Ni-Cr alloys	8000	n.a.	200	220	490–830	35	180	15	13	500	85
AL-6X	N08366	24Ni-21Cr-6.5Mo-2Mn-1Si	Fe-Ni-Cr alloys	n.a.		n.a.	210–240	515	10–30	n.a.	n.a.	n.a.	n.a.	n.a.
AL-6XN	N08367	24Ni-21Cr-3.5Mo-2Mn-1Si	Fe-Ni-Cr alloys	n.a.		n.a.	315	715	30	n.a.	n.a.	n.a.	n.a.	n.a.
Alloy® 20Mo-4	N08024	38Ni-32Fe-24Cr-4Mo-1Cu	Fe-Ni-Cr alloys	8106		186	262	615	41	155	14.9	12.1	458	105.6
Astroloy® M	N13017	54.8Ni-15Cr-17Co-5.3Mo-4Al-3.5Ti	Ni-Cr alloys	7910		n.a.	1050	1410	16	n.a.	n.a.	n.a.	n.a.	n.a.
Carpenter® 20Cb-3	N08020 W88021	35Ni-38Fe-20Cr-3Cu-2Mo-1Nb	Fe-Ni-Cr alloys	8080		n.a.	240–414	550–655	30	184	14.7	12.2	500	108.2
Carpenter® 20Mo-6	N08026	46Fe-35Ni-24Cr-6Mo-3Cu	Fe-Ni-Cr alloys	8133		186	275	607	50	n.a.	14.8	12.1	460	108.2
Cromifer® 1025	N08925	20Ni-25Cr-6.5Mo-2Mn-1Si-1Cu	Fe-Ni-Cr alloys	n.a.		n.a.	300	600	40	n.a.	n.a.	n.a.	n.a.	n.a.
Duranickel® 301	N03301	94Ni-4.5Al-0.5Ti	Low alloy	8250	1400–1440	207	207–862	655–1170	25–55	346	13.0	23.8	435	42.5
Hastelloy® B	N10001 W80001	64Ni-28Mo-1Cr-5Fe-1Si	Ni-Mo alloys	9240	n.a.	n.a.	n.a.	600–980	<60	100–230	10.3	11.1	n.a.	n.a.
Hastelloy® B2	N10665 W80665	69Ni-28Mo-2Fe-1Cr-1Co-1Mn-0.1Si	Ni-Mo alloys	9220		217	3	914–955	53–55	235	10.3	11.1	373	137
Hastelloy® B3	N10675	65Ni-28.5Mo-3Co-3W-3Mn-1.5Fe-1.5Cr-0.5Al-0.2Ti-0.1Si	Ni-Mo alloys	9220	1370–1418	216	400	885	57.8	n.a.	10.6	11.2	373	137

Hastelloy® C4	N06455 N26455	65Ni-16Mo-16Cr-3Fe-2Co-1Mn- 0.7Ti	Ni-Mo alloys	8640	n.a.	211	416	768		52	184		10.8	10.1	406	125
Hastelloy® C22	N06022 W86022	56Ni-22Cr-13Mo-3Fe-3W-2.5Co- 0.5Mn-0.35V	Ni-Cr-Mo alloys	8690	1357- 1399	206	372	785		62	209		12.4	10.1	414	114
Hastelloy® C276	N10276 W80276	57Ni-16Mo-16Cr-5Fe-4W-2.5Co- 1Mn-0.35V	Ni-Mo-Cr-Fe alloys	8890	1323- 1371	205	355- 415	758- 790		50-61	185		11.2	10.2	427	130
Hastelloy® C2000	N06200	59Ni-23Cr-16Mo-1.6Cu	Ni-Cr-Mo alloys	8500	n.a.	209	358- 372	752- 779		62-68	n.a.		12.4	9.1	n.a.	128
Hastelloy® G3	N06985	44Ni-22Cr-19.5Fe-7Mo-2Cu	Ni-Cr-Fe alloys	8140	1260- 1343	199	320- 379	690- 724		40-50	184		12.2	14.3	452	107.5
Hastelloy® G30	N06030	43Ni-30Cr-15Fe-5Mo-5Co-3W- 1.5Mn	Ni-Cr-Fe-Mo alloys	8220		202	310	689		56-65	90 HRB		12.8	10.2	n.a.	116
Hastelloy® HX	N06920	48.3Ni-22Cr-18.5Fe-9Mo-1.5Co	Ni-Cr-Fe alloys	8230	1260- 1355	205	358	793		46	184		13.3	11.6	461	116
Hastelloy® N	n.a.	71Ni-16Mo-7Cr-5Fe-1Si-0.8Mn	Ni-Mo-Cr alloys	8860	1300- 1400	219	314	794		50.7	96-99 HRB		11.6	11.5	419	120
Hastelloy® S	N06635	67Ni-16Cr-15Mo-3Fe-2Co-1W	Ni-Cr-Fe alloys	8750	1335- 1380	212	445	835		49	168		11.5	14.0	398	128
Hastelloy® X	N06002 W86002	47Ni-22Cr-18Fe-9Mo-1.5Co-0.6W- 1Mn-1Si-0.1C	Ni-Cr-Fe alloys	8220	1260- 1355	205	339- 385	755- 1110		43	150-280 87-92 HRB		13.9	9.1	486	118
Haynes® HR120	N12120	37Ni-33Fe-25Cr-3Co-2.5Mo-2.5W- 0.7Nb-0.7Mn-0.6Si-0.05C-0.004B	Ni-Fe-Cr-Co alloys	8070	1300	197	375	735		50	n.a.		14.3	11.4	467	105.2
Haynes® HR160	N12160	37Ni-30Co-28Cr-2.75Si-3.5Fe- 1Mo-1Nb-1W-0.5Mn-0.5Ti-0.05C	Ni-Co-Cr alloys	8080	1293- 1370	211	314	767		68	n.a.		13.0	10.9	462	111.2
Haynes® 214	N12140	75Ni-16Cr-4.5Al-3Fe-0.5Mn-0.2Si- 0.1Zr-0.05C-0.01B-0.01Y	Ni-Cr-Al-Fe alloys	8050	1355- 1400	218	605	995		36.8	24 HRC		13.3	12.0	452	135.9
Haynes® 230	N06230	57Ni-22Cr-14W-2Mo-5Co-3Fe- 0.5Mn-0.4Si-0.3Al-0.1C-0.02La	Ni-Cr-W-Mo alloys	8970	1301- 1371	211	390	860		48	200		12.7	8.9	397	125
Haynes® 242	n.a.	65Ni-25Mo-8Cr-2.5Co-2Fe-0.8Mn- 0.8Si-0.5Al-0.5Cu-0.03C-0.006B	Ni-Mo-Cr alloys	9050	1290- 1375	229	845	1290		33.7	n.a.		10.8	11.3	386	122
Haynes® 556	n.a.	31Fe-20Ni-22Cr-18Co-3Mo-3W	Fe-Ni-Cr alloys	8230		205	410	815		47	91		14.6	11.1	464	95.2

Table 2.37. (continued)

Common and trade name	UNS	Average chemical composition (/ wt.%)	Class	Density (ρ /kg.m ⁻³)	Melting point or range (°C)	Young's modulus (E/GPa)	Yield strength 0.2% proof (σ_{ys} /MPa)	Ultimate tensile strength (σ_{UTS} /MPa)	Elongation (Z/%)	Brinell hardness (/HB)	Coef. linear thermal exp. ($\alpha/10^{-6}$ K ⁻¹)	Thermal conductivity (k/W.m ⁻¹ .K ⁻¹)	Specific heat capacity (cP/J.kg ⁻¹ .K ⁻¹)	Electrical resistivity ($\rho/\mu\Omega$.cm)
Incoloy® 800	N08800	46Fe-32.5Ni-21Cr-0.4Al-0.35Ti-0.05C	Fe-Ni-Cr alloys	7940	1357–1385	193	295–345	590–621	40–45	138–180	14.4	11.5	460	98.9
Incoloy® 800HT	N08811	46Fe-33Ni-21Cr-0.4Al-0.35Ti-0.08C	Fe-Ni-Cr alloys	7940	1357–1385	193	241–310	552–600	44–45	138–180	14.4	11.5	460	98.9
Incoloy® 825	N08825	42Ni-22Cr-28Fe-3Mo-2Cu-1Mn-0.8Ti-0.05C	Fe-Ni-Cr alloys	8140	1370–1400	206	310	655–690	45	150	14.0	11.1	440	113.0
Incoloy®902	N09902	42Fe-42Ni-5Cr-2.5Ti-1Si-0.5Al	P-H Ni superalloys	8050	1318–1393	n.a.	760	1210	25	300	7.6	12.1	502	101
Incoloy®903	N19903	42Fe-38Ni-15Co-3Nb-1.5Ti-0.6Al	P-H Ni superalloys	8250	1318–1393	n.a.	1100	1310	14	n.a.	7.65	16.7	435	61.0
Incoloy®907	N19907	42Fe-38Ni-13Co-4.7Nb-1.5Ti-0.2Al-0.2Si	P-H Ni superalloys	8330	1335–1400	n.a.	1100	1310	14	n.a.	7.7	14.8	431	69.7
Incoloy®909	N19909	42Fe-38Ni-13Co-4.7Nb-1.5Ti	P-H Ni superalloys	8300	1395–1430	159	1035	1275	15	n.a.	7.7	14.8	427	72.8
Incoloy® 925	N09925	44Ni-28Fe-21Cr-3Mo-1.8Cu-2Ti-0.3Al	P-H Fe-Ni superalloys	8080	1311–1366	199	815–827	1172–1210	24	315	13.2	13.9	435	116.6
Inconel® 600	N06600	74.5Ni-15.5Cr-8Fe-1Mn-0.5Si-0.5Cu	Ni-Cr-Fe alloys	8470	1354–1413	214	172–345	550–690	35–55	120–150	13.3	15.9	444	103
Inconel® 601	N06601	60.5Ni-23Cr-14Fe-1.5Al-1Cu	Ni-Cr-Fe alloys	8110	1360–1411	206.5	205–415	550–790	40–70	110–150	13.75	11.2	448	118
Inconel® 601GC	N06601	60.5Ni-24Cr-11Fe-1.25Al-1Cu-1Mn-1Si-0.16Zr-0.04N	Ni-Cr-Fe alloys	8110	1301–1368	205	205–345	585–690	35–55	n.a.	14	11	448	118
Inconel® 603XL	N06603	74Ni-19Cr-4Mo-2Si-0.5Ti-0.5Al-0.1REE	Ni-Cr-Mo alloys	8540	1380–1400	219	410	795	50	n.a.	12.87	11	439	116

Inconel® 617	N06617	52Ni-22Cr-12.5Co-9.5Mo-1.5Fe-1.2Al-0.1C	Ni-Cr-Fe alloys	8360	1332-1380	211	322-383	734-769	56-62	173	11.6	13.6	419	122
Inconel® 625	N06625	62Ni-21Cr-5Fe-9Mo-3.7 (Nb+Ta)-1Co-0.5Mn-0.4Ti-0.4Al	Ni-Cr-Fe alloys	8440	1290-1350	208	448-517	862-930	42-45	186	12.8	9.8	410	129
Inconel® 625LCF	N06626	59Ni-22Cr-9Mo-5Fe-4Nb-0.4Al-0.4Ti	Ni-Cr-Mo-Fe alloys	8440	1290-1350	208	414	827	40	n.a.	12.8	9.7	410	129
Inconel® 686	N06686	57Ni-20.5Cr-16.3Mo-3.9W-1Fe	Ni-Cr-Mo-W alloys	8730	1338-1380	207	396	740	60	n.a.	11.97	9.8	373	123.7
Inconel® 690	N06690	58Ni-30Cr-10Fe-0.5Mn-0.5Si-0.5Cu	Ni-Cr-Fe alloys	8190	1343-1377	211	348-461	648-758	39-52	175	14.1	13.5	450	114.8
Inconel® 693	N06693	60Ni-29Cr-5Fe-3Al-1Mn-1Ti-0.5Cu-0.5Si	Ni-Cr-Fe-Al alloys	7770	1317-1367	196	490-530	883-938	42-45		13.04	9.1	455	117
Inconel® 718	N07718	52.5 (Ni+Co)-19Cr-18.8Fe-5.2Nb-3.1Mo-1Co-0.9Ti-0.5Al	P-H Ni superalloys	8190	1260-1336	216	1036-1180	1240-1350	17-20	331	13.0	11.4	435	125
Inconel® 718SPF	n.a.	55 (Ni+Co)-19Cr-5 (Nb+Ta)-3Mo-1Ti-1Al-1Co	Ni-Cr-Nb-Mo alloys	8190	1260-1335	216	829	1117	31	24 HRC	12.2	11.1	435	125
Inconel® 725	N07725	59Ni-22.5Cr-9.5Mo-4Nb-3Fe-1.7Ti-0.35Al	Ni-Cr-Mo-Nb alloys	8310	1271-1343	204	427-921	855-1268	30-60	5-39 HRC	13.0	10.6	430	114
Inconel® 740	n.a.	55Ni-25Cr-20Co-2Nb-1.8Ti-0.9Al-0.7Fe-0.5Mo	Ni-Cr-Co-Nb alloys	8050	1288-1362	221	314	795	58	n.a.	12.38	10.2	449	117
Inconel® 751	N07751	70 (Ni+Co)-15Cr-7Fe-2.3Ti-1.2Al-1 (Nb+Ta)-1Mn-0.5Cu-0.5Si	Ni-Co-Cr-Fe alloys	8220	1390-1430	214	516-976	554-1310	18-26	173-352	12.6	12	n.a.	122
Inconel® 783	R30783	35Co-28Ni-26Fe-3Cr-3Nb-5Al	Co-Ni-Fe alloys	7810	1336-1407	178	779	1194	24	n.a.	10.1	10.1	455	n.a.
Inconel® MA 754	N07754	78Ni-20Cr-1Fe-0.6Y ₂ O ₃ -0.5Ti-0.3Al	P-H Ni superalloys	8550	1400	203	545-585	940-965	20-22	n.a.	12.5	14.3	440	108
Inconel® MA 758	n.a.	70Ni-30Cr-0.6Y ₂ O ₃	P-H Ni superalloys	8140	1375	205	560	949	27	n.a.	12.47			114
Inconel® X-750	N07750	73 (Ni+Co)-16Cr-7Fe-2.5Ti-0.7Al-1 (Nb+Ta)	P-H Ni superalloys	8280	1393-1427	207	690-900	1137-1240	20	382	12.6	12.0	425	122

Table 2.37. (continued)

Common and trade name	UNS	Average chemical composition (/ wt.%)	Class	Density (ρ /kg.m ⁻³)	Melting point or range (/°C)	Young's modulus (E/GPa)	Yield strength 0.2% proof (σ_{ys} /MPa)	Ultimate tensile strength (σ_{UTS} /MPa)	Elongation (Z/%)	Brinell hardness (/HB)	Coef. linear thermal exp. (α /10 ⁻⁶ K ⁻¹)	Thermal conductivity (k/W.m ⁻¹ .K ⁻¹)	Specific heat capacity (cP/J.kg ⁻¹ .K ⁻¹)	Electrical resistivity (ρ /μΩ.cm)
Invar®36	K93601	64Fe-36Ni	Fe-Ni low exp. alloys	8100	1430	140	275–415	450–585	30–45	160	1.5	10	515	80
Invar®42	K94100	48Fe-52Ni	Fe-Ni low expansion alloys	8100	1435	144	235	538	32	160	5.3	10.5	515	61
Invar® 48	K94800	52Fe-48Ni	Fe-Ni low expansion alloys	8200	1450	160	260	520	43	80 HRB	8.5	16.7		47
Invar® K	K94610	53Fe-30Ni-17Co	Fe-Ni low expansion alloys	8160	1450	130	340	520	42	83 HRB	6.0	16.7		43
Invar® 77	n.a.	77Ni-13.5Fe-5Cu-4Mo	Fe-Ni low expansion alloys	8770	n.a.			530–550		86 HRB				
JS-700	N08700	25Ni-21Cr-5Mo-2Mn-1Si	Fe-Ni-Cr alloys	n.a.	n.a.	n.a.	240	550	30	n.a.	n.a.	n.a.	n.a.	n.a.
Monel® 400	N04400	63(Ni+Co)-32Cu-2.5Fe-2.0Mn-0.5Si	Ni-Cu (Cupronickels)	8830	1300–1350	179	172–345	517–620	35–60	110–150	14.2	24	427	51.1
Monel® 401	N04401	54Cu-42.5Ni-0.75Fe-2.25Mn-0.25Si-0.25Co	Ni-Cu (Cupronickels)	8910	1300–1350	169	134	441	51	43	13.7	21	n.a.	49.8
Monel® 404	N04404	55(Ni+Co)-44Cu-0.5Fe-0.1Mn-0.1Si	Ni-Cu (Cupronickels)	8910	1300–1350	169	152	469	50	44	13.6	21	414	49.8
Monel® R-405	N04405	63(Ni+Co)-31Cu-2Mn	Ni-Cu (Cupronickels)	8910	1300–1350	180	172–276	482–586	35–50	110–140	14.2	22	427	51.2
Monel® K-500	N05500	63Ni-30Cu-2.75Al-2Fe-1.5Mn-1.2Ti	Ni-Cu (Cupronickels)	8440	1315–1350	180	689–790	1069–1100	25–30	290–300	13.7	17.2	419	61.8
Nimonic® 75	N06075	76Ni-20Cr-2Fe-1Si-1Mn-0.4Ti	P-H Fe-Ni superalloys	8370	1340–1380	221	240	750	40	170	11.0	11.7	461	109

Nimonic® 80A	N07080	69Ni-19.5Cr-3Fe-2.4Ti-2Co-1.4Al-1Mn-1Si	P-H Fe-Ni superalloys	8190	1320–1355	222	480–793	900–1241	30	370	12.7	11.2	448	124
Nimonic® 81	N07081	63Ni-30Cr-2Co-1.8Ti-1Fe-0.9Al-0.5Mn-0.5Si-0.06Zr	P-H Fe-Ni superalloys	8060	1305–1375	212	565	1200	38	n.a.	11.1	10.9	461	127
Nimonic® 86	n.a.	Ni-25Cr-10Mo-0.05C-0.03Ce-0.015Mg	P-H Fe-Ni superalloys	8540	n.a.	210	438	873	45	n.a.	12.7	n.a.	n.a.	n.a.
Nimonic® 90	N07090	58Ni-20Cr-16Co-2.5Ti-1.5Fe-1Mn-1Si-0.15Zr	P-H Fe-Ni superalloys	8180	1310–1370	226	752	1175	30	380	12.7	11.47	446	118
Nimonic® 91	n.a.	43Ni-29Cr-20Co-2.3Ti-1.3Al-1Fe-1Mn-1Si-0.8Nb-0.1Zr	P-H Fe-Ni superalloys	8080	1300–1350	222	663	1180	31.2	n.a.	n.a.	n.a.	447	n.a.
Nimonic® 105	N07105	51Ni-15Cr-20Co-5Mo-5Al-1.2Ti-1Fe-1Si-0.15Zr	P-H Fe-Ni superalloys	8010	1290–1345	223	776	1140	22	380	12.2	10.89	419	131
Nimonic® 115	N07115	55Ni-15Cr-13Co-4Mo-5Al-4Ti-1Fe-1Mn-1Si-0.15Zr	P-H Fe-Ni superalloys	7850	1260–1315	216	865	1240	27	400	12.0	10.6	444	139
Nimonic® 263	N07263	51Ni-20Cr-20Co-6Mo-2Ti-0.7Fe-0.5Al	P-H Fe-Ni superalloys	8360	1300–1355	224	585	1004	39	320	11.1	11.72	461	115
Nimonic® 901	N09901	42.5Ni-5Fe-12.5Cr-35.75Mo-2.9Ti-1Co	P-H Fe-Ni superalloys	8140	1280–1345	201	900	1220	15	n.a.	13.5	n.a.	431	112
Nimonic® PE11	n.a.	65Fe-39Ni-18Cr-5.25Mo-2.35Ti-1Co-0.85Al-	P-H Fe-Ni superalloys	8020	1280–1350	200	700	1070	20	n.a.	n.a.	n.a.	436	n.a.
Nimonic® PE16	n.a.	44Ni-16.5Cr-32Fe-3.3Mo-2Co-1.2Ti-1.2Al	P-H Fe-Ni superalloys	8000	1310–1355	198	450	830	37	280	11.8	11.72	544	110
Nimonic® PK33	n.a.	55Ni-18Cr-14Co-7Mo-2.25Ti-2.1Al-1Fe	P-H Fe-Ni superalloys	8210	1300–1345	221	790	1127	30	n.a.	10.6	11.3	419	126
Rene® 41	N07041	55.4Ni-19Cr-12Co-10.5Mo-5Fe-1.6Al-3.2Ti	P-H Ni superalloys	8250	1232–1391	218	1060	1420	14	n.a.	13.6	11.9	452	130.8
Rene® 95	n.a.	61.5Ni-14Cr-8Co-3.5Mo-3.5Nb-3.5Al-2.5Ti	P-H Ni superalloys	n.a.	n.a.	n.a.	1310	1620	15	n.a.	n.a.	8.7	n.a.	n.a.
Sanicro® 28	N08028	31Ni-27Cr-2Mn-1Si	Fe-Ni-Cr alloys	n.a.	n.a.	n.a.	215	500	40	n.a.	n.a.	n.a.	n.a.	n.a.
Udimet®500	N07500	53.7Ni-18Cr-18.5Co-4.0Mo-2.9Ti-2.9Al	P-H Ni superalloys	8020	n.a.	n.a.	840	1310	32	n.a.	n.a.	11.1	n.a.	120.3

Table 2.37. (continued)

Common and trade name	UNS	Average chemical composition (/ wt.%)	Class	Density (ρ /kg.m ⁻³)	Melting point or range (°C)	Young's modulus (E/GPa)	Yield strength 0.2% proof (σ_{ys} /MPa)	Ultimate tensile strength (σ_{UTS} /MPa)	Elongation (Z/%)	Brinell hardness (/HB)	Coef. linear thermal exp. (α /10 ⁻⁶ K ⁻¹)	Thermal conductivity (k/W.m ⁻¹ .K ⁻¹)	Specific heat capacity (cP/J.kg ⁻¹ .K ⁻¹)	Electrical resistivity (ρ /μΩ.cm)
Udimet®520	n.a.	56Ni-19Cr-12Co-6.25Mo-3Ti-2Al-1W	P-H Ni superalloys	8210	1260–1405	n.a.	850	1300	20					
Udimet®700	N07700	55.5Ni-15Cr-17Co-5Mo-4Al-3.5Ti	P-H Ni superalloys	7910	n.a.	n.a.	965	1410	17	n.a.	n.a.	19.6	n.a.	n.a.
Udimet®720	n.a.	57Ni-16Cr-15Co-5Ti-3Mo-2.5Al-1.25W	P-H Ni superalloys	8080	1194–1338	n.a.	900	1150	9	n.a.	6.8	n.a.	n.a.	n.a.
Ultimet®	R31233	54Co-26Cr-9Ni-5Mo-3Fe-2W-0.8Mn-0.3Si	Co-Cr alloys	8470	1332–1334	215	545	1024	36	296 HV	13.0	12.3	456	87
Waspaloy®	N07001	53Ni-19.5Cr-13.5Co-4.3Mo-4.25Ti-1.4Al-2Fe-1Mn-0.75Si	P-H Ni superalloys	8190	1330–1360	211	795	1275	25	n.a.	11.7	10.7	n.a.	124

Trademark owners: Duranickel®, Incoloy®, Inconel®, Monel®, and Permalnickel® (International Nickel Company, Inco); Hastelloy® (Haynes International); MAR-M® (Martin Marietta); Pyromet® (Carpenter Technology); Rene® (General Electric); Rene 41® (Allvac Metals); Nimonic® and Udimet® (Special Metals); Waspaloy (United Aircraft)

2.2.7 Nickel-Titanium Shape Memory Alloys

2.2.7.1 History

The *shape memory effect* was first reported in 1932 by the Swedish physicist Arne Ölander, who observed the pseudoelastic behavior of the gold-cadmium alloy¹⁰. Later, Greninger and Mooradian observed the formation and disappearance of a martensitic phase by decreasing and increasing the temperature of a Cu-Zn alloy. But it remained a scientific curiosity until the 1960s, when Buehler and coworkers at the U.S. Naval Ordnance Laboratory discovered the shape memory effect in a quasiequiatom alloy of nickel and titanium (55Ni-45Ti). This alloy was later named NiTiNOL after the acronym for *Nickel-Titanium Naval Ordnance Laboratory*. Since that time, intensive investigations have been conducted to elucidate the strange behavior of this alloy. The use of NiTiNOL for medical applications was first reported in the 1970s, but it was only in the mid-1990s, however, that the first widespread commercial stent applications made their breakthrough in medicine.

2.2.7.2 Fundamental

A NiTiNOL shape memory metal alloy can exist in two different temperature-dependent crystal structures or phases called martensite (i.e., lower-temperature phase) and austenite (i.e., higher-temperature or parent phase). Several properties of the austenite and martensite phases are notably different. When martensite is heated, it begins to change into austenite. The temperature at which this phenomenon starts is called the *austenite start temperature* (A_s). The temperature at which the phenomenon is complete is called the *austenite finish temperature* (A_f). When austenite is cooled, it begins to change into martensite. The temperature at which this phenomenon starts is called the *martensite start temperature* (M_s). The temperature at which martensite is again completely reverted is called the *martensite finish temperature* (M_f). Composition and metallurgical treatments have dramatic impacts on the above transition temperatures. From the point of view of practical applications, NiTiNOL can have three different forms:

- (i) martensite;
- (ii) stress-induced martensite (i.e., superelastic);
- (iii) austenite.

When the material is in its martensite form, it is soft and ductile and can be easily deformed like tin pewter. Superelastic NiTiNOL is highly elastic, while austenitic NiTiNOL is quite strong and hard, similar in that way to titanium metal. The NiTi material has all these properties, their specific expression depending on the temperature at which it is used.

The temperature range for the martensite-to-austenite transformation, i.e., soft-to-hard transition, that occurs upon heating is higher than that for the reverse transformation upon cooling. The difference between the transition temperatures upon heating and cooling is called hysteresis. In practice, hysteresis is generally defined as the difference between the temperatures at which a material is 50% transformed into austenite upon heating and 50% transformed into martensite upon cooling. This temperature difference can be as high as 20 to 30°C. Therefore, in order to transform NiTiNOL by body temperature upon heating ($A_f < 37^\circ\text{C}$), it must cool down to about +5°C to fully retransform into martensite (M_f).

The unique behavior of NiTiNOL is based on the temperature-dependent austenite-to-martensite phase transformation on an atomic scale, which is also called thermoelastic martensitic transformation. The thermoelastic martensitic transformation causing the shape

¹⁰ Ölander, A. (1932) *J. Am. Chem. Soc.*, **54**, 3819

Table 2.38. Properties of the 55Ni-45Ti shape memory alloy

Structure type	Density ($\rho/\text{kg.m}^{-3}$)	Melting point ($\text{mp}/^\circ\text{C}$)	Young's or elastic modulus (E/GPa)	Yield strength 0.2% proof ($\sigma_{0.2}/\text{MPa}$)	Ultimate tensile strength (σ_{UTS}/MPa)	Elongation ($Z/\%$)	Thermal conductivity ($k/\text{W.m}^{-1}\text{.K}^{-1}$)	Coefficient of linear thermal expansion ($\alpha/10^{-6}\text{K}^{-1}$)
Austenitic	6450	1300	83	195–690	895	25–50	18	11
Martensitic	6450	1300	28–41	70–140	1900	5–10	8.6	6.6

recovery is a result of the need of the crystal lattice structure to accommodate to the minimum energy state for a given temperature. In NiTiNOL, the relative symmetries between the two phases lead to a highly ordered transformation, where the displacements of individual atoms can be accurately predicted and eventually lead to a shape change on a macroscopic scale.

2.2.7.3 Shape Memory Effect

NiTiNOL reacts to any change in ambient temperature and hence is able to convert its shape into a preprogrammed structure. To exhibit shape memory, an object is deformed at low temperatures (i.e., the martensitic condition) and maintained in this state. Upon heating, the object attempts to return to its original state (i.e., the austenitic condition). Superelastic 55Ni-45Ti tubes can be bent ten times more than steel tubes without kinking or collapsing. This is called the one-way shape memory effect. The ability of shape memory alloys (SMAs) to recover a preset shape upon heating above the transformation temperatures and to return to a certain alternate shape upon cooling is known as the two-way shape memory effect. Two-way memory is exceptional. There is also an all-round shape memory effect, which is a special case of the two-way shape memory effect.

2.2.7.4 Superelasticity

Superelasticity, or pseudoelasticity, refers to the ability of NiTiNOL to return to its original shape upon unloading after a substantial deformation. This is based on stress-induced martensite formation. The application of an external stress causes martensite to form at temperatures higher than M_s . The macroscopic deformation is accommodated by the formation of martensite. When the stress is released, the martensite reverts to austenite and the specimen returns to its original shape. Superelastic NiTiNOL can be strained several times more than ordinary metal alloys without being plastically deformed, which reflects its rubberlike behavior. This is, however, only observed over a specific temperature area. The highest temperature at which martensite can no longer be stress induced is denoted by M_d . Above M_d NiTiNOL is deformed like ordinary materials by slipping. Below A_s , the material is martensitic and does not recover. Thus, superelasticity appears in a temperature range from near A_f up to M_d . The largest ability to recover occurs close to A_f .

2.2.7.5 Fabrication

Nickel-titanium solid SMAs are manufactured by a double-vacuum melting process to ensure the quality, purity, and properties of the final material. After the formulation of raw materials, the alloy is vacuum-induction melted at 1400°C . After the initial melting, the alloy transition temperature must be controlled due to the sensitivity of the transition temperature to small changes in the alloy chemistry. This is followed by vacuum-arc remelting to

improve the chemistry, homogeneity, and structure of the alloy. Double-melted ingots can be hot worked at 800°C and cold worked to a wide range of product sizes and shapes. Porous NiTiNOL can be made by sintering or using *self-propagating high-temperature synthesis* (SPHS), also called ignition synthesis.

2.2.8 Major Nickel Producers

Table 2.39. Major nickel producers

Company	Address
BHP Billiton Ltd.	180 Lonsdale Street, Melbourne Victoria 3000, Australia Telephone: (61) 1300 55 47 57 Fax: (61 3) 9609 3015 URL: http://www.bhpbilliton.com/
Norilsk Nickel	22 Voznesensky Pereulok, Moscow, 125993, Russia Telephone: (495) 787 7667 Fax: (495) 785 5808 URL: http://www.nornik.ru/
Vale Inco	200 Bay Street, Royal Bank Plaza Suite 1600, South Tower P.O. Box 70, Toronto, Ontario, Canada M5J 2K2 Telephone: (416) 361-7511 Fax: (416) 361-7781 E-mail: inco@inco.com
Sherritt Gordon Mines Ltd.	1133 Yonge Street, Toronto, ON M4T 2Y7, Canada Telephone: (416) 924 4551 Fax: (416) 924 5015 URL: http://www.sherritt.com/

2.3 Cobalt and Cobalt Alloys

2.3.1 Description and General Properties

Cobalt [7440-48-4], chemical symbol Co, atomic number 27, and relative atomic mass 58.933200(9), is an element of group VIII B(9) of Mendeleev's periodic chart. Cobalt is a brittle and hard grayish-white metal similar to iron and nickel, the other elements of the iron triad. But once polished it exhibits a faint bluish tint. Cobalt has two allotropes, a low-temperature epsilon phase (ϵ -Co) with a hexagonal close-packed arrangement of atoms, and above a transition temperature of 422°C it converts to the alpha phase (α -Co) with a face-centered cubic structure¹¹. The ϵ -Co allotrope has a density of 8900 kg.m⁻³. Like iron and nickel, cobalt is a soft ferromagnetic material but with a lower saturation magnetization M_s of 1.42×10^6 A.m⁻¹, and it exhibits the highest Curie temperature known of 1121°C, above which it loses its ferromagnetism and becomes paramagnetic. Its melting point is 1493°C and

¹¹ The two allotropes of cobalt were designated in the order of their discovery. Therefore the room temperature, hcp, was originally called alpha and the medium temperature, fcc, was named beta. In modern nomenclature, the hcp phase was named epsilon, but the reader must always keep in mind that alpha may refer either to hexagonal or cubic cobalt.

Table 2.40. Reactions of cobalt metal with acids

Acid	Soln.	Chemical reaction scheme	Notes
Hydrochloric acid (HCl)	dil. hot	$\text{Co}^0 + 2\text{HCl} \longrightarrow \text{Co}^{2+} + 2\text{Cl}^- + \text{H}_2(\text{g})$	Dissolves slowly
Sulfuric acid (H_2SO_4)	Dil. hot	$\text{Co}^0 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Co}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	Dissolves slowly
Nitric acid (HNO_3)	Dil.	$3\text{Co}^0 + 8\text{HNO}_3 \longrightarrow 3\text{Co}^{2+} + 6\text{NO}_3^- + 2\text{NO}(\text{g}) + 4\text{H}_2\text{O}$	Dissolves readily
	Conc.	$3\text{Co}^0 + 16\text{HNO}_3 + 16\text{H}^+ \longrightarrow \text{Co}_3\text{O}_4(\text{surface}) + 8\text{NO}_2(\text{g}) + 8\text{H}_2\text{O}$	Dissolve extremely slowly due to passivation by Co_3O_4

it retains its strength to a high temperature, which explains its uses in cutting tools, superalloys, surface coating, high-speed steels, cemented carbides, and diamond tooling. Molten cobalt vaporizes at 3100°C . The electronic structure of the ground state of the atom $[\text{Ar}]3\text{d}^7 4\text{s}^2$ leads to cobalt's commonest valency, i.e., Co^{2+} , by removal of the two 4s electrons. Other valencies exist, however, in some complex salts, and mixed valencies occur in Co_3O_4 , for example (Co^{2+} and Co^{3+}). The major reactions of cobalt metal with most common acids are summarized in Table 2.40.

Cobalt imparts to silicate melts intense blue colors used in glassmaking, glazes, and enamels. From a biological point of view, cobalt is one of the world's essential elements. Actually, as one of the 27 elements that are essential to humans, cobalt occupies an important role as the central component of cyanocobalamin (vitamin B12). Industrially, two grades of commercially pure cobalt are available on the market: (i) cobalt (99.3 wt.% Co), used for noncritical metallurgical applications, in the chemical industry, and for permanent magnets and catalysts, while (ii) cobalt (99.8 wt.% Co) is used in rechargeable lithium ion batteries and fine chemicals.

Prices (2006). Pure cobalt (99.8 wt.%) is priced US\$32.19/kg (US\$14.60/lb.).

2.3.2 History

The use of cobalt goes back to 2000 to 3000 years before the common era (B.C.E.). Although it had not been identified, the addition of cobalt minerals to glass to impart the traditional cobalt blue color was already known. In the 16th century, the term *kobold* denoted malicious spirits (gnomes) who frequented mines. This term was then extensively used as a nickname in the Erzgebirge region of Saxony (i.e., Schneeberg and Hartz Mountains) for certain sulfide ores that were difficult to smelt. Actually, these regions were important silver mining areas, and when smelting failed to yield copper or silver and emitted noxious arsenic trioxide fumes during roasting, causing some respiratory problems with the miners, these issues were all attributed to kobold. The calcined obtained and mixed with silica sand was called *zaffre*. The fusion of *zaffre* with potash (K_2CO_3), or ground soda glass, produced a potash or soda silica glass with blue color called smalt. The blue color obtained was first attributed erroneously by alchemists to arsenic and bismuth. Cobalt metal was first isolated by the Swedish chemist Georg Brandt in 1735. However, the main use of cobalt remained as a coloring agent until the 20th century, and in fact, before World War I, cobalt was really only available or used as an oxide. Its modern uses arose with the work of Elwood Haynes on cobalt-chromium-tungsten wear-resistant alloys first commercialized under the tradename Stellite®, and later with the development of Alnico® magnets in Japan and the use of cobalt metal as a binder for tungsten-carbide particles in hardmetal (WC-Co) in Germany.

2.3.3 Natural Occurrence, Minerals and Ores

Cobalt is not a particularly rare chemical element, with an abundance in the Earth’s crust of 25 mg/kg, which places it together with lithium and niobium. It is, however, widely scattered in rocks but is found in potentially exploitable quantities in several countries (Table 2.41). Significant sources of cobalt also exist in the deep-sea polymetallic nodules and crusts that occur in the midocean ridges in the Pacific and are estimated to contain anywhere from 2.5 to 10 million tonnes of cobalt. According to the U.S. Geological Survey, in 2004 world resources were ca. 15 million tonnes. The main cobalt minerals are sulfides and sulfosalts and, to a lesser extent, oxidized compounds such as oxides, carbonates, and sulfates. As a sulfide, cobalt occurs combined with copper in *carrolite* [CuCo₂S₄, cubic], which is found in the Democratic Republic of Congo and Tanzania, and with nickel in *siegenite* [(Ni,Co)₃S₄, cubic], which is found in cobaltiferous ore deposits near Fredrictown in the Southern Missouri lead district. Cobalt occurs alone as sulfide in *linnaeite* [Co₃S₄, cubic], which is found in the Democratic Republic of Congo, or in the Mississippi Valley Pb-Zn deposits. The cobalt arsenides such as *safflorite* [CoAs₃, orthorhombic] are found in North America, in Morocco, and in other parts of the world, while *skutterudite* [CoAs₃, cubic] is found in Morocco. Sulfoarsenides such as *cobaltite* [CoAsS, orthorhombic] are found in Canada in the Cobalt district of Ontario, in the Blackbird region of Idaho, in Australia, in Myanmar, and in other localities worldwide. Oxidized cobalt minerals include *asbolane* [(Ni,Co)_xMn(O,OH)₄·nH₂O, hexagonal], which is found in lateritic nickel ore

Table 2.41. Cobalt-producing countries (2004)	
Country	Production (tonnes)
Australia	4000
Botswana	Unknown
Brazil	1000
Belgium	1200
Canada	4000
China	5500
Cuba	Unknown
France	180
Finland	8000
India	260
Japan	350
Morocco	1200
New Caledonia	
Norway	4500
Russia	4500
South Africa	250
Uganda	
DRC	1200
Zambia	6500
Total =	43,000
Source: The Cobalt Development Institute (CDI)	

deposits such as those of New Caledonia, the *heterogeneite* [$\text{CoO}(\text{OH})$, hexagonal], which is the principal mineral of the Democratic Republic of Congo, and finally as sulfates in *bieberite* [$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, monoclinic]. Primary cobalt is only extracted alone from arsenide ores found in Morocco, Canada, and Idaho, but usually primary cobalt is extracted as a by-product during the processing of nickel and copper ores and, to a lesser extent, from the processing of zinc ores (e.g., India) and precious metals¹². In 2003, about 44% of world production came from nickel ores (i.e., laterites and sulfides). Secondary sources of cobalt metal are from metallic products reentering the cobalt cycle such as turnings from the machining of cobalt-based superalloys, spent catalysts, spent samarium-cobalt magnets, and finally used hardmetal cutting tools (i.e., cemented carbides). In 2004, according to the Cobalt Development Institute, ca. 50,000 tonnes of cobalt metal were produced worldwide. In 2005, the major companies producing cobalt worldwide were, in order of decreasing annual production capacity, the 100 Chinese producers (12,700 tonnes), the American producer OMG (8164 tonnes) and the Canadian producer Vale Inco (6350 tonnes), Norilsk Nickel (4990 tonnes) in Russia, and finally Chambashi Metals (3630 tonnes) in Zambia.

2.3.4 Processing and Industrial Preparation

2.3.4.1 Cobalt as a Byproduct of Nickel Processing

Cobalt can be recovered from nickel-sulfide concentrates or nickel matte by the Sherritt-Gordon ammonia leaching process in Fort Saskatchewan, Alberta, Canada, and it is also recovered from sulfuric-acid pressure leaching of laterites. In both cases, cobalt is obtained in nickel-free liquor by reduction with hydrogen under elevated pressure and temperature (Section 2.2).

2.3.4.2 Electrowinning of Cobalt

Table 2.42. Electrowinning of cobalt metal	
Parameters	Value
Anode material	Pb-Ca-Sn
Cathode materials	Stainless steel 316L
Diaphragm	Undivided cell
Electrolyte composition	Co^{2+} 45 g/L pH = 3.7
Operating temperature	55–58°C
Total current	13 kA
Current density	0.5 kA.m ⁻²
Cell voltage	
Faradic efficiency	85
Specific energy consumption	6.5 kWh/kg

¹² Hawkins, M.L. (1998) Recovering cobalt from primary and secondary sources. *J. Mater.*, **50**(10), 46–50.

2.3.5 Properties of Cobalt Alloys and Superalloys

Superalloys are usually defined as heat- and oxidation-resistant alloys specially developed for servicing at elevated temperatures under both oxidizing atmosphere and severe mechanical stresses. Three main classes of superalloys are distinguished:

- (i) *iron-based superalloys* (Section 2.1.17);
- (ii) *nickel-based superalloys* (Section 2.2.6);
- (iii) *cobalt-based superalloys*, discussed here.

Historically, the development of cobalt-based superalloys has been driven by the jet engine. However, their use has extended into many other fields such as all types of turbines, space vehicles, rocket engines, nuclear-power reactors, thermal power plants, and, recently, the chemical-process industry (CPI), where these alloys are used especially for their hot corrosion resistance. The role of cobalt is not completely understood, but it certainly increases the useful temperature range of nickel-based alloys. Phase γ' also occurs as γ'' , which has a body-centered tetragonal structure (i.e., two stacked cubes). Cobalt is thought to raise the melting point of this phase, thereby enhancing high-temperature strength. In addition to structure, processing has been responsible for enhancing these alloys. Cobalt alloys are called austenitic because the high-temperature face-centered cubic crystal lattice is stabilized at room temperature. They are hardened by carbide precipitation; thus carbon content is a critical parameter. Chromium provides oxidation resistance, while other refractory metals are added to give solid-solution strengthening (e.g., tungsten and molybdenum) and to promote the formation of carbide (e.g., tantalum, niobium, zirconium, and hafnium). Because oxygen content is deleterious, the processing of cobalt alloys requires melting in a vacuum. Moreover, tight specifications make it necessary to prevent an excess of solid-solution metals such as W, Mo, and Cr that tend to form unwanted and deleterious phases similar to the nickel alloys and Laves phases (Co_3Ti). Cobalt alloys obtained by powder metallurgy exhibit a finer carbide dispersion and a smaller grain size and hence have superior properties to cast alloys. Further process development by hot isostatic pressing (HIP) has even further improved the properties by removal of possible failure sites. Compared to nickel alloys, the stress rupture curve for cobalt alloys is flatter and shows lower strength up to about 930°C, which is explained by the greater stability of the carbides. This factor is the primary reason for using cobalt alloys in the lower-stress, higher-temperature stationary regime for gas turbines. Casting is important for cobalt-based superalloys, and directionally solidified alloys have led to increased rupture strength and thermal fatigue resistance. Even further improvements in strength and temperature resistance have been achieved by the development of single-crystal alloys. Both these trends have allowed the development of higher-thrust jet engines, which operate at even higher temperatures. The cast and wrought cobalt superalloys, despite the better properties of the γ' -hardened nickel-based alloys, continue to be used for the following reasons:

- (i) Cobalt alloys are more heat resistant than nickel- or iron-based superalloys owing to their higher liquidus temperature.
- (ii) They have a higher chromium content, which leads to a superior oxidation resistance to the harsh atmosphere found in gas turbine operations.
- (iii) Cobalt superalloys show superior thermal fatigue resistance and weldability over nickel alloys. The physical, mechanical, thermal, and electrical properties of selected commercial cobalt alloys (mainly stellites) are listed in Table 2.43.

Stellite® 1	R30001	Co-31Cr-12.5W-3Ni-3Fe-2.4C-2Si-1Mo-1Mn	8690	n.a.	618	<1	51-58	1255-1290	n.a.	n.a.	10.5	94
Stellite® 3	R0003	Co-30Cr-13W-3Ni-3Fe-2.4C-2Si-1Mo-1Mn	8640		618	<1	51-58	1250-1280				
Stellite® 4	R30004	Co-30Cr-14W-3Ni-3Fe-2Si-1Mo-1Mn-0.57C	8600	618	1010	<1	45-49	1260-1330			9.5	
Stellite® 6	R30006	Co-28Cr-4.5W-3Ni-3Fe-2Si-1.2C-1Mo-1Mn	8460	541	896	1	30-43	1285-1395	n.a.	n.a.	11.35	84
Stellite® 7	R30007	Co-26Cr-6W-0.4C	8130	461	932	8	30-35	1260-1415			11.0	
Stellite® 8	R30008	Co-30Cr-6Mo-0.2C	8100	490	932	9	30-35	1186-1383			11.0	
Stellite® 12	R30012	Co-29Cr-8.3W-3Ni-3Fe-2Si-1.8C-1Mo-1Mn	8630	647	834	<1	47-51	1280-1315			11.5	
Stellite® 12P	R30012	Co-31Cr-9W-3Ni-3Fe-2Si-1.4C-1Mo-1Mn	8560	618	883	<1	43-48	1280-1315	n.a.	n.a.	11.35	88
Stellite® 20	R30020	Co-33Cr-18W-2.5C	9000	618	n.a.	<1	55-59	1260-1265			10.0	
Stellite® 21	R30021	Co-28Cr-5.5Mo-2.5Ni-2Fe-2Si-1Mn-0.25C	8340	494	694	9	32	1186-1383	n.a.	n.a.	11.5	88
Stellite® 100	R30100	Co-34Cr-19W-2C	8690	432	n.a.	<1	61-66	1150-1190			10.0	
Stellite® 306	R30306	Co-25Cr-6Nb-5Ni-2W-0.4C	n.a.	n.a.	n.a.	n.a.	36	n.a.				
Stellite® X-40	R30040	Co-25Cr-10Ni-7W-0.3C	8610	431	735	10	30-35	1260-1415			10.5	
Stellite® SF1	n.a.	Co-19Cr-13Ni-13W-3Si-2.5B-1C	8230	n.a.	n.a.	n.a.	54-58	1069-1180			9.15	
Stellite® SF6	n.a.	Co-19Cr-13Ni-8W-2.5Si-1.5B-1C	8320	373	627	n.a.	43-46	1085-1150			9.50	
Stellite® SF12	n.a.	Co-19Cr-13Ni-9W-2.5Si-1.5B-1C	8350	n.a.	n.a.	n.a.	48-50	1061-1104			9.20	
Stellite® SF20	n.a.	Co-19Cr-15W-13Ni-3Si-3B-1.5C	8350	n.a.	n.a.	n.a.	60-62	1010-1215			11.25	
Tantung G	n.a.	Co-30Cr-16.5W-7Ni-5Fe-4.5(Nb+Ta)-3Mn-3C	8300	n.a.	585-620	n.a.	60-63	1150-1200	26.8	n.a.	4.2	n.a.

NB: For stellite alloys the Young's or elastic modulus is between 180 and 249 MPa; the bulk or compression modulus is between 152 and 296 MPa; the Coulomb's or shear modulus is between 90 and 97 MPa.

2.3.6 Corrosion Resistance of Stellites

In nitric (HNO₃) and acetic acid (CH₃COOH), all grades of stellite are highly corrosion resistant at room temperature because they passivate. In hydrochloric acid (HCl), the stellite alloys behave in a similar manner to austenitic stainless steels. In sulfuric acid (H₂SO₄), certain stellite grades (e.g., 1, 4, 6, 8, and 12) also possess a good resistance to chemical attack, but other grades are prone to severe pitting (e.g., SF1, SF2, SF12, and SF40). Stellite alloys also possess a high resistance to oxidation in superheated steam over 538°C, and hence they are extensively used for seats and rubbing surfaces in valves. Regarding oxidation resistance, tests conducted at 700 to 800°C in burnt oil fuel gases containing vanadium pentoxide (V₂O₅) showed that the oxidation rate of stellite alloys is ca. 2.2 mm per year. This must be compared with 9 mm/year for AISI 304 stainless steel and 350 μm/year for AISI 310 stainless steel. In air, the cobalt-based alloys possess good resistance to oxidation at high temperatures. At 800°C, for instance, only a thin adherent oxide film is formed. At higher temperatures, the rate increases, but even at 1000°C it does not reach scaling proportions. Continuous exposure of stellite alloys at 400°C in carbon dioxide results in little discoloration of the surface, and at 600°C there is an increase in weight of about 20 mg.m⁻².d⁻¹. Regarding corrosion by liquid metals, bulk stellite and stellite-faced components are extensively used in diecasting machines handling zinc- and tin-based alloys. When selecting a stellite alloy to operate in zinc above 425°C care must be taken as some grades are strongly attacked. Cobalt-based stellite alloys are attacked by molten aluminum to various degrees, but laboratory tests showed that they compare favorably with high-silicon cast-iron and chrome vanadium die steel. In liquid mercury, the cobalt-based alloys are unattacked up to 250°C. In contact with liquid sodium or potassium, the cobalt-based alloys exhibit a good resistance to both metals and their alloys (e.g., NaK) up to 800°C. In molten lithium, they show satisfactory resistance up to 300°C, but they are attacked at higher temperatures. Finally, Stellite® 7 is used for gravity die casting of molten brass, but Stellite® 1 is rapidly attacked at 1050°C. Stellite alloys are attacked by molten bismuth.

2.3.7 Industrial Applications and Uses

Table 2.44. Uses of selected stellite grades	
Grade	Description and uses
Stellite® 1 Stellite® 3 Stellite® 20	Possess high abrasion and corrosion resistance for applications such as pump sleeves and rotary seal rings, wear pads, bearing sleeves, and centerless grinder work rests. All are available as castings; Stellite® 1 and Stellite® 20 are available for hardfacing.
Stellite® 4 Stellite® 12 Stellite® 12P	Alloys having greater wear resistance than Stellite® 6 and used for applications subject to less mechanical shock. Stellite® 4 is a machinable casting alloy having extremely good high-temperature strength and is used for dies for hot pressing and the hot extrusion of copper-based and aluminum alloys. Stellite® 12 is a machinable hardfacing alloy used for facing the cutting edges of long knives employed in the carpet, plastics, paper, and chemical industries.
Stellite® 6 Stellite® 306	Less ductile than Stellite® 7, 8, and X-40 but more resistant to wear and having good resistance to impact. Used in the form of castings and welded deposits on steam and chemical valves and as welded deposits on equipment handling hot steel, such as shear blades, tong bits, guides, etc. Stellite® 306 is a cobalt-based wire designed for use in conditions of thermal and mechanical shock.

Table 2.44. (continued)

Grade	Description and uses
Stellite® 7 Stellite® 8 Stellite® X-40	Casting alloys possessing excellent corrosion resistance and high-temperature strength together with good ductility and excellent resistance to thermal shock. Used for gas turbine blades, brass casting dies, and extrusion dies. All are machinable.
Stellite® 100	The hardest and most abrasion-resistant Stellite, designed specifically for metal-cutting purposes and used in the form of tool bits, tips, milling cutter blades, etc. Also available for small solid components of simple design where maximum wear resistance is required. Possesses good corrosion resistance and the highest hot hardness. Not machinable.
Stellite® F6	Hardfacing alloy for application by the thermal spraying and powder-weld processes giving a machinable deposit of similar hardness to Stellite® 6.
Stellite® SF12	Hardfacing alloy for application by the thermal spraying and powder-weld processes giving a machinable deposit of similar hardness to Stellite® 12.
Stellite® SF1 Stellite® SF20	Hardfacing alloys for application by the thermal spraying process giving deposits of similar hardness to Stellite® 1 and Stellite® 20. Stellite® SF1 can also be deposited by powder welding and is machinable; Stellite® SF20 must be ground.
Reference: Collective (1970) <i>Properties of Deloro Stellite® Alloys</i> . Deloro Stellite, Belleville, ON, Canada	

2.3.8 Major Cobalt Producers

Table 2.45. Major cobalt producers

Company	Address
Chambashi Metals	URL: http://www.chambishimetals.com
Norilsk Nickel	22 Voznesensky Pereulok, Moscow, 125993, Russia Telephone: (495) 787 7667 Fax: (495) 785 5808 URL: http://www.nornik.ru/
OM Group	127 Public Square, 1500 Key Tower, Cleveland, OH 44114-1221, USA Telephone: (216) 781-0083 Fax: (216) 781-1502 URL: http://www.omgi.com/
Vale Inco	200 Bay Street, Royal Bank Plaza Suite 1600, South Tower P.O. Box 70, Toronto, Ontario, Canada M5J 2K2 Telephone: (416) 361-7511 Fax: (416) 361-7781 E-mail: inco@inco.com

2.4 Manganese and Manganese-Based Alloys

2.4.1 Description and General Properties

Manganese [7439-96-5], chemical symbol Mn, atomic number 24, and relative atomic mass 54.938049(9), is the first element of group VIIB(7) of Mendeleev's periodic chart. Its name is derived from the Latin word *magnes*, owing to the magnetic properties of pyrolusite

Table 2.46. Physical properties of four manganese allotropes

Properties (SI units)	α -Mn	β -Mn	γ -Mn	δ -Mn
Crystal structure	Complex cubic	Complex cubic	fcc	bcc
Lattice parameters (/pm)	$a = 891.39$	$a = 631.45$	$a = 386.24$	$a = 308.10$
Space group (Hermann–Mauguin)	I43 m	P4 ₃ 2	Fm3 m	Im3 m
Pearson symbol	cI58	cP20	cF4	cI2
Strukturbericht	A12	A13	A1	A2
Transition temperature (T/K)	973	1361	1412	1519 (<i>m.p.</i>)
Latent enthalpy of transition (ΔH /kJmol ⁻¹)(MJ.kg ⁻¹)	2226 (40.52)	2122 (38.63)	1879 (34.20)	12058 (219.48)
Density (ρ /kg.m ⁻³)	7440	7290	7210	6057
Coefficient of linear thermal expansion ($\alpha/10^{-6}$ K ⁻¹)	22.3	24.9	14.8	41.6
Thermal conductivity (k/W.m ⁻¹ .K ⁻¹)	7.8			
Specific heat capacity (c_p /J.kg ⁻¹ .K ⁻¹)	477	482	502	861
Electrical resistivity ($\rho/\mu\Omega$.cm)	160–185	90–44	40–60	

(see Section 2.4.2). It is a silvery-grayish-white and brittle metal very similar to iron but lighter and harder. It exhibits a density ranging from 7210 to 7440 kg.m⁻³ depending on its allotropic forms. Actually, the pure metal exhibits four allotropes. Alpha manganese (α -Mn) is stable at room temperature up to 700°C and exhibits a complex cubic structure; it then transforms into beta manganese (β -Mn) with another complex cubic crystal lattice. At 1088°C, gamma manganese (γ -Mn), with a face-centered cubic structure, is a soft variety able to be cut and bent. Above 1139°C, delta manganese (δ -Mn), with a body-centered cubic lattice, forms up to the metal's melting point of 1246°C. Manganese metal vaporizes at 2061°C. Selected physical properties of the four manganese allotropes are listed in Table 2.46. At cryogenic temperatures, manganese metal is antiferromagnetic; however, above its Néel temperature of 100 K it becomes paramagnetic with a mass magnetic susceptibility of $+1.21 \times 10^{-7}$ m³/kg. Manganese can become ferromagnetic only after special treatment. Manganese is a mononuclidic element with only one stable nuclide ⁵⁵Mn.

From a chemical point of view manganese exhibits numerous oxidation states from Mn(-III) to Mn(VII), with divalent Mn(II) being the most stable. At room temperature, pure manganese metal is not attacked by oxygen, nitrogen, or hydrogen. However, at high temperatures it reacts vigorously with oxygen, sulfur, and phosphorus. For these reasons, it is used industrially in iron- and steelmaking as a powerful reducing, desulfurizing, and dephosphorizing agent forming stable dioxide (MnO₂), sulfide (MnS), or phosphide (MnP), respectively. Manganese dissolves readily in acids with the evolution of hydrogen and formation of manganous salts. Hot concentrated sulfuric acid dissolves manganese with the evolution of sulfur dioxide (SO₂), while nitric acid is decomposed with simultaneous evolution of H₂, N₂, and NO. Manganese dioxide is dissolved by hydrochloric acid with the evolution of nascent chlorine gas. The major reactions of manganese metal with most common acids are summarized in Table 2.47.

Prices (2006). Pure manganese is priced US\$1.28/kg (US\$0.58/lb.).

Table 2.47. Reactions of pure manganese metal with acids

Acid		Chemical reaction scheme	Notes
Acetic acid (CH ₃ COOH)	Conc.	$\text{Mn}^0 + 2\text{CH}_3\text{COOH} \longrightarrow \text{Mn}^{2+} + 2\text{CH}_3\text{COO}^- + \text{H}_2(\text{g})$	Dissolves
Hydrochloric acid (HCl)	Conc.	$\text{Mn}^0 + 2\text{HCl} \longrightarrow \text{Mn}^{2+} + 2\text{Cl}^- + \text{H}_2(\text{g})$	Dissolves
Sulfuric acid (H ₂ SO ₄)	Dil.	$\text{Mn}^0 + \text{H}_2\text{SO}_4 \longrightarrow \text{Mn}^{2+} + \text{SO}_4^{2-} + \text{H}_2(\text{g})$	Dissolves forming pink solution of manganous cations
	Conc. hot	$\text{Mn}^0 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Mn}^{2+} + \text{SO}_4^{2-} + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}$	
Nitric acid (HNO ₃)	Dil. hot	$3\text{Mn}^0 + 8\text{HNO}_3 \longrightarrow 3\text{Mn}^{2+} + 6\text{NO}_3^- + 2\text{NO}(\text{g}) + 4\text{H}_2\text{O}$	Dissolves
	Conc. cold	$\text{Mn}^0 + 4\text{HNO}_3 \longrightarrow \text{Mn}^{2+} + 2\text{NO}_3^- + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}$	Dissolves

2.4.2 History

During prehistoric times, earthy mixtures of manganese and iron oxides were used during the Paleolithic as raw color pigments for the painting of caves. Later, during ancient times, around A.D. 50, Pliny the Elder described ore deposits of pyrolusite located near the town of Magnesia in Asia Minor. Because of its magnetic properties, at that time the mineral was called by its Latin name, *magnesia negra*, to distinguished it from another magnetic mineral, *lapis magnesia* (i.e., magnetite). Pyrolusite was used by Egyptians and Romans as a decolorizing additive in glassmaking in order to control the color. Actually, minute additions of manganese dioxide removes by a redox reaction the green-yellowish coloration imparted by impurities of ferrous iron, while larger amounts impart a pink, purple, or even black hue. During the 1400s, the German name *braunstein* denoted various manganese ores without distinguishing their chemical composition. In the mid-17th century, the German chemist Glauber obtained potassium permanganate (KMnO₄), and nearly a century later powdered manganese dioxide heated with *muriatic acid* (hydrochloric acid) became the basis for the manufacture of chlorine gas. The element was first recognized in 1774 by the Swedish chemist Carl Wilhelm Scheele in 1771, and the same year his collaborator Johan Gottlieb Gahn isolated the impure metal by direct reduction of pyrolusite with charcoal. But the metal was first named manganese by Buttman only in 1808. In 1826, Prieger in Germany produced ferromanganese with 80 wt.% Mn, while pure Mn metal was produced by J.M. Hearsh in 1840. In 1841, *spiegeleisen*, a Mn-rich variety of pig-iron containing 20 wt.% Mn was first produced in France by Pourcel. Later, following the work of Sir Henry Bessemer in developing the steelmaking process, especially for removing deleterious sulfur and oxygen, the use of ferromanganese as a desulfurizing and dephosphorizing agent was patented by Sir William Siemens in 1866. Finally, in 1875, Pourcel began industrial production of ferromanganese with 65 wt.% Mn, while in a totally different area, Leclanché in France invented in 1868 the first dry cell using manganese dioxide mixed with carbon as a negative, moistured salmiac (ammonium chloride) as electrolyte and a zinc metal foil as anode. In 1882, the first electric ferromanganese was produced in an electric arc furnace (EAF). Finally, industrial production of manganese metal by an aluminothermic process was launched in 1898.

2.4.3 Natural Occurrence, Minerals, and Ores

Manganese is the twelfth most abundant element in the Earth's crust (950 mg/kg), but the element is highly dispersed to form primary manganese ore deposits. It appears in a variety of minerals species, ca. 100, among which about a dozen are commonly found: sulfides such as *alabandite* [MnS, cubic]; oxides such as *pyrolusite* [MnO₂, tetragonal], *haussmanite* [Mn₃O₄, tetragonal], and *jacobsite* [MnFe₂O₄, cubic]; hydroxides such as *manganite* [γ -MnOOH, monoclinic], *romanechite* (formerly *psilomelane*) [(Ba,Mn)₃Mn₈O₁₆(OH)₆, monoclinic], and *cryptomelane* [KMnMn₈O₁₆]; carbonates such as *rhodochrosite* [MnCO₃, trigonal]; silicates such as *rhodonite* [(Mn,Fe,Ca)SiO₃, triclinic], *braunite* [3Mn₂O₃·MnSiO₃, tetragonal], *tephroite* [Mn₂SiO₄, orthorhombic], and *spessartite* [Mn₃Al₂(SiO₄)₃, cubic]; and even titanates such as *pyrophanite* [MnTiO₃, trigonal]. The word *wad* is a general name for a soft earthy and hydrated mixture of manganese and iron oxides.

From a metallogenic point of view, four types of manganese ore deposits can be distinguished:

- (i) Ore deposits due to the weathering of mafic igneous rocks, but these are of little commercial importance.
- (ii) Stratiform or lenticular sedimentary deposits originating from the weathering of igneous parent rocks and finally marine deposition of precipitated oxides, hydroxides, and carbonates. Oxide deposits formed in areobic (oxidizing) conditions exhibit higher grades of manganese ores (25 to 40 wt.% Mn), while carbonate deposits formed in anaerobic (reducing) conditions are often mixed with clays and limestones and hence have a lower manganese content (15 to 30 wt.% Mn). These deposits are found in South Africa (Kalahari fields).
- (iii) Supergene lateritic deposits made of a residual sedimentary rock originated from *in situ* superficial alteration in humid tropical conditions of rich manganese carbonated rocks. Later, alteration products are depleted from soluble cations (e.g., Na, K, Ca, Mg) by the leaching action of water. Hence, insoluble cations such as Mn(III), Fe(III), and Al(III) associated with clays and silica remain in the materials. Such deposits are found in Brazil (Amapá), Ghana (Nsuta), and Gabon (Moanda).
- (iv) Hydrothermal manganese deposits in epithermal and mesothermal veins, where manganese dioxide forms the gangue along with calcite and quartz of metallic sulfide veins with sphalerite (ZnS), galena (PbS), chalcopyrite (CuFeS₂), and gold (Au).
- (v) As well as in land-based deposits, manganese is also found in **polymetallic nodules** lying on the deep ocean floor (seabeds) at a depth of ca. 5 km. Actually, polymetallic nodules contain on average 25 wt.% Mn along with 1 wt.% Ni together with copper. Nodules with an especially high metal content are found in the northern equatorial Pacific Ocean. Offshore deep mining is difficult and would be very expensive, but during the 1970s and early 1980s high hopes for future commercial mining were expressed due to their high nickel and copper content. But these nodules are now seen as potentially valuable resources for the long-term future.

From a mining point of view, deposits of economic interest must contain manganese ores with more than 35 wt.% Mn to be considered profitable, although some commercially mined deposits, especially in the CIS, India, and China, are well below this level. As well as the ore grade, mineral hardness and the presence of other elements such as copper, cobalt, phosphorus, sulfur, and arsenic is important in determining the viability of the ore body for development.

According to the U.S. Geological Survey, if only high-grade manganese ores with a minimum of 44 wt.% Mn are considered, the world reserves of manganese are estimated at around 680×10^6 tonnes (excluding seabed resources), while if 35 wt.% Mn is retained, reserves reach

700×10^6 tonnes, both contained in a reserve base of 5×10^9 tonnes. Three quarters of these reserves are located in Australia, Brazil, South Africa (Kalahari field), and Ukraine (Nikopol area), while Gabon accounts for 7% of world reserves. Other deposits have also been mined in Ghana and India but are now exporting only limited quantities of low- or medium-grade ore. The ore mined in Mexico is mostly for domestic use, but part of it is exported in the form of manganese nodules. The world's largest known land-based manganese deposit, consisting of sedimentary manganese ore interlaid with ironstone, is located in the Northern Cap Province of South Africa and is called the Kalahari field. Today ca. 74% of manganese mining and 48% of world ferromanganese-alloy production is shared by Australia, Brazil, Gabon, and South Africa; a lesser proportion is shared by Ghana, India, Mexico, Ukraine, CIS, and China. The western world's production is accounted for by four companies: Samancor (RSA), Eramet (Belgium), CVRD (Brazil), and Assmang (RSA). The world production of manganese ore and concentrates is estimated to be 17×10^6 tonnes.

Prices (2006). Metallurgical-grade manganese ore (48 wt.% Mn) is priced US\$0.26/kg of Mn contained.

2.4.4 Processing and Industrial Preparation

2.4.4.1 Mining and Beneficiation of Manganese Ores

Manganese ores are generally beneficiated by crushing, washing, and screening. Standard manganese content of ores is ca. 48%. Roasting and reduction of suitable ores may be carried out to increase the manganese oxide content, giving rise to “battery”- or “chemical”-grade material. World production of contained manganese is about 7.2×10^6 tonnes. Approximately 74% of manganese mining and 48% of ferromanganese-alloy production in the western world in 2000 was under the control of four producers: Samancor, Eramet, CVRD, and Assmang. World production of manganese ore and concentrates in gross weight terms fell from 26 Mt in 1990 to 18 Mt in 1998, as a result of declines in Ukraine, Australia, Brazil, and India.

Table 2.48. Major manganese ore concentrate producers

Producer	Plant location	annual Production (10^6 tonnes)
Samancor	South Africa Australia	6.55
Eramet	France Gabon United States Norway China	1.79
Compahnia do Valle do Rio Doce (CVRD)	Brazil France	1.65
Assmang	South Africa	1.40
Total		11.39

2.4.4.2 Preparation of Pure Manganese Metal

Manganese metal was first produced by an aluminothermic process in 1898 (see History). Some commercial production took place in the early 20th century. At present, two major techniques are used industrially to produce pure manganese metal on a large commercial

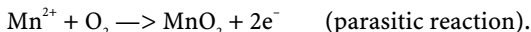
scale: electrowinning from aqueous manganous sulfate electrolytes and electrothermal-silicothermic reduction or arc smelting of manganese ores.

Electrowinning of aqueous manganous electrolytes. Electrowinning in aqueous electrolytes was first invented by Davis in 1930, but commercial production was pioneered by the former US Bureau of Mines (USBM) in the late 1930s. However, the process spread around the world and became significant only after World War II in the 1950s when US, Japanese, and South African companies implemented the process industrially. Electrowinning is the most important process for producing high-purity manganese metal sold as “flakes” (which are the stripped cathode deposits) or as powder (i.e., at least 99.9 wt.% Mn). The electrolytic process comprises three steps.

- (i) **Ore comminution and reduction.** To ensure a high chemical reactivity during both reduction and leaching operations, the ore is crushed and ball-milled with 90 wt.% passing 200 mesh (75 μm). Then the high-surface-area powdered ore is hot reduced into a rotary kiln at 800 to 1000°C with a combination of various reductants such as anthracite coal, charcoal, oil, natural gas, and coal gas. The reduction ensures that all the Mn(IV) that is refractory to attack by acids will be entirely converted into the water-soluble manganous species Mn(II). During the reduction, other metallic cations are also reduced, especially ferric iron, which ends as ferrous Fe(II) or even metallic iron. The level of Fe(II) is a good indicator of the completion of the reduction of manganese. During discharge of the kiln, the reduced calcined ore must not be oxidized again and is cooled below 100°C.
- (ii) **Leaching and iron removal.** The reduced calcined ore is mixed with spent sulfuric acid electrolyte (2 to 5 wt.% H_2SO_4). Manganous cations dissolve along with Fe(II) and must be removed prior to electrowinning. After an air oxidation treatment that converts all ferrous iron to ferric iron, the pH is raised above 2, ensuring the precipitation of $\text{Fe}(\text{OH})_3$, along with $\text{Al}(\text{OH})_3$ and entrained silica (SiO_2). Moreover, other deleterious transition metals such as cobalt and nickel are removed as insoluble metal sulfides, adding sodium sulfide and adjusting the pH. After completion the final liquor contains ca. 10 wt.% MnSO_4 .
- (iii) **Electrowinning of metal.** Electrowinning is performed in a divided electrolyzer with a polymer diaphragm as separator to prevent the anodic oxidation of manganous cations, leading to the unwanted formation of manganese dioxide. Cathodes are made of stainless steel or titanium while lead-silver or lead-calcium anodes are used. However, these are now replaced by dimensionally stable anodes for oxygen evolution made of titanium coated with an electrocatalyst of mixed metal oxides such as $\text{Ta}_2\text{O}_5\text{-IrO}_2$. The electrochemical reactions are described below. At the cathode the electrodeposition of pure manganese metal is:



while at the anode the evolution of oxygen occurs:



The performances of the electrolyzer are listed in Table 2.49. Once electrodeposited, the 2-mm-thick manganese plates are stripped from the base metal substrate by mechanical shock due to the brittleness of the alpha-manganese deposit. The removed metal flakes are washed and dried. The absorbed hydrogen is removed by heating under inert atmosphere to produce pure manganese metal with a low interstitial oxygen content. Approximately 150,000 tonnes of electrolytic manganese metal were produced in 2004.

Table 2.49. Electrowinning of manganese metal

Parameters	Value
Anode material	Pb-Ag or Pb-Ca, DSA-IrO ₂
Cathode materials	Stainless steel or titanium
Diaphragm	Polymer fabric
Electrolyte composition	MnSO ₄ 4wt.% (NH ₄) ₂ SO ₄ 13 wt.% SO ₂ or SeO ₂ pH = 7.0 Smoothing additives
Operating temperature	35–45°C
Anodic current density	1 kA.m ⁻²
Cathodic current density	0.5 kA.m ⁻²
Cell voltage	5 V to 7 V
Faradic efficiency	42–62 %
Specific energy consumption	9–12 kWh/kg

Table 2.50. Electrolytic manganese grades (ASTM B 601)

ASTM grades	UNS	wt.% Mn	wt.% S	H	N
Grade A	M29450	99.5	0.030 max	0.015	–
Grade B	M29952	99.5	0.030 max	0.005	–
Grade C	M29953	99.5	0.030 max	0.0001	–
Grade D	M29450	94–95	0.035 max	–	4.0–5.4
Grade E	M29350	93–94	0.035 max	–	5.5–6.5
Grade F	M29954	99.5	0.035 max	0.0030	–

The major producers of electrolytic manganese worldwide are Erachem Comilog and Kerr-McGee Chemical in the United States, the Manganese Metal Company (MMC) in the Republic of South Africa, and finally Mitsui Mining & Smelting and Tosoh in Japan.

Electrothermal-silicothermic reduction process. In 1966, electrothermic manganese, with a purity ranging between 93 and 98 wt. % Mn, was first produced on a commercial scale in France by P  chiney. The process uses high-silicon silicomanganese to yield extremely low carbon levels. Manganese ore is smelted in an electric arc furnace (EAF with silicomanganese as reductant. This slagging process produces a low-grade ferromanganese with a high phosphorus content.

2.4.4.3 Ferromanganese and Silicomanganese

Ferromanganese (Fe-Mn-C). The extractive metallurgy of manganese is very similar to iron-making except that a higher temperature, over 1200°C, is required for the carbothermic reduction of manganese dioxide. Standard or high-carbon ferromanganese, which is to manganese what pig iron is to iron, is a very commonly used alloy. It contains more than 76 wt.% Mn and various levels of carbon content (i.e., high carbon ca. 7.5 wt.% C, medium carbon 1 to 1.5 wt.% C, and low carbon <1 wt.% C) and can be produced either by smelting manganese oxidic ores in the blast furnace or in the electric arc furnace and subsequent oxygen refining to reduce the carbon content. In 2000, the production worldwide reached 3.4×10^6 tonnes.

Prices (2006). High-carbon-grade is priced US\$0.85–0.90/kg and medium-grade manganese is priced US\$1.2–1.4/kg.

Silicomanganese (Si-Mn-C). Another high-tonnage alloy is silicomanganese, which was first produced in the early 20th century, when calcium-carbide furnaces were reconverted to produce ferroalloys. Silicomanganese contains typically 65 to 85 wt.% Mn, 14 to 16% Si, and 2 wt.% C. It is produced in a calcium-carbide furnace through the addition of quartz in the smelting of manganese oxidic ore. Lower carbon levels result when the silicon content is increased. Special grades with up to 30 wt.% Si are produced for use in the manufacture of stainless steel. In 2000, worldwide production of Si-Mn was about 3.5×10^6 tonnes.

Prices (2006). Lump material containing 65 to 75 wt.% Mn is priced US\$0.85–0.90/kg.

2.4.5 Industrial Applications and Uses

2.4.5.1 Metallurgical Uses

The steel industry accounts for ca. 90% of world demand for manganese. Carbon steel is the principal market, accounting for 70% (i.e., 4×10^6 tonnes) of manganese consumption. Actually, manganese is extensively used in iron- and steelmaking because of its desulfurization ability and its powerful deoxidation capacity. Roughly 30% of the manganese used today in steelmaking is as desulfurization and deoxidation agent, while the remaining 70% of the manganese is used purely as an alloying element. Actually, manganese is an austenite stabilizer, despite its not being as powerful as nickel, though it is much less expensive. The effect of manganese in forming austenite can be reinforced by combining it with nitrogen, which is also an austenite-forming element. Manganese also increases hardenability rates. For instance, high-strength low-alloy steels with yield strengths above 500 MPa contain over 1 wt.% Mn. Manganese-rich stainless steels (i.e., AISI 200 series), are low-cost stainless steels where nickel is replaced partly or entirely by manganese. Finally, small amounts of manganese are used in aluminum alloys for enhancing its corrosion resistance.

2.4.5.2 Nonmetallurgical Uses

Batteries. The most important nonmetallurgical application of manganese is in the form of manganese dioxide (MnO_2), which is used as a cathodic depolarizer (i.e., positive or cathode material) in Leclanché dry-cell ($\text{Zn}/\text{NH}_4\text{Cl}/\text{MnO}_2$), alkaline batteries ($\text{Zn}/\text{KOH}/\text{MnO}_2$), and, to a lesser extent, lithium batteries (Li/MnO_2). Zinc primary cell consumption worldwide exceeds 20 billion units annually. *Natural manganese dioxide* (NMD) can be used in dry cells only, and its market is ca. 180,000–200,000 tonnes per year. Nevertheless, very few ores exhibit the properties required for the manufacture of dry cells. The major countries producing NMD are Gabon, Ghana, Brazil, China, Mexico, and India. For alkaline batteries and other high-performance cells, purer manganese-dioxide grades are required and should be obtained synthetically. *Activated manganese dioxide* (AMD) is obtained after roasting at 600°C of high-grade oxidic manganese ores, and the calcined product is then treated with sulfuric acid. *Chemical manganese dioxide* (CMD), which is mainly composed of $\delta\text{-MnO}_2$, is in fact regarded as a *manganite*, that is, an alkali metal manganate (IV) (MMn_2O_6). It is usually produced by the reduction of potassium permanganate with manganous salts. *Electrochemical manganese dioxide* (EMD) is made through electrolysis of a manganous sulphate electrolyte. Combined production of both synthetic types is ca. 200,000 tonnes per year.

Chemicals. Potassium permanganate (KMnO_4) is one of the best known manganese products. It is a powerful oxidizing agent with bactericidal and algicidal properties, which enable it to be used in purifying drinking water and treating waste water. It is also used for odor control, including deodorization of discharges from paint factories, fish-processing plants, etc. Permanganate has a variety of other applications as an oxidant.

Table 2.51. Industrial uses of manganese

Application	Description
Iron- and steelmaking (91%)	Manganese is introduced as an additive into blast and electric furnaces, where it has a dual purpose as a desulfurization and deoxidizing agent (representing 30% of use in steelmaking) and as an alloying agent to improve hardness (accounting for 70% of use in steelmaking). Manganese is added mainly either as ferromanganese or silicomanganese, but also occasionally in its metallic form. The choice of form in which manganese is added depends upon the steel being produced and, hence, desired carbon and silicon content.
Primary and secondary batteries (4%)	Manganese dioxide (MnO_2), in natural, chemical, or electrochemical grade, is used as cathode material in dry-Leclanché cells and alkaline batteries.
Chemical industries (3%)	A variety of manganese compounds are used in a wide range of applications including glassmaking, animal feed, human nutrient supplements, gasoline additives, oxidant in water and wastewater treatment, dyes, rust proofing, inks, chlorination catalysts, and paint dryers.
Alloying element (2%)	Pure manganese metal is used as an alloying element to increase strength, toughness, hardness, and the rate of transformation. It is used mainly in aluminum alloys to make aluminum cans but also in copper, silver, and other nonferrous metals.

2.4.6 Major Manganese Producers

Table 2.52. Major producers of manganese metal

Country	Manganese producer
Australia	Consolidated Minerals
Brazil	Companhia Vale Do Rio Doce (CVRD) Mineracao Buritirama
China	Guangxi Bayi Ferroalloy Co. Shanghai Jinneng International Trade Co. Shanxi Jiaocheng Yiwang Ferroalloy Plant Sichuan Chuantou Emei Ferroalloy Co.
France	Eramet Comilog Manganese
Ghana	Ghana Manganese Co.
Japan	Chuo Denki Kogyo Co. Mizushima Ferroalloy Co. Nippon Denko Co.
Kazakhstan	JSC Zhayremsky GOK
Korea	Dongbu Hannong Chemical Co.
Norway	Tinfos Jernverk A/S
Slovak Republic	OFZ a.s
South Africa	Highveld Steel & Vanadium Corp. Ore & Metal Co. Samancor
Spain	Grupo Ferroatlantica
Ukraine	JSC Nikopol Ferroalloy Plant Ukraine